Institute of Paper Science and Technology

CHEMICAL RECOVERY

PROJECT ADVISORY COMMITTEE

DECEMBER 14, 1990

IPST

Atlanta, Georgia

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL RECOVERY

PROJECT ADVISORY COMMITTEE

December 14, 1990

CHEMICAL RECOVERY
PROJECT ADVISORY COMMITTEE

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11/28/90

Chemical Recovery Project Advisory Committee

of

The Institute of Paper Science and Technology

December 14, 1990 Meeting

Atlanta, Georgia

AGENDA

8:30	Welcome	- Armstrong, Empie
8:35	Goals/Objectives	- Yeske
9:00	Recovery PAC Organization	- Armstrong
9:30	Program Summary	- Empie
9:45	Project Review	- Group
12:00	Lunch/Tour	
1:00	Project Reviews	- Group
3:00	Discussion	- Committee
4:00	Adjournment	- Armstrong

A190 TOPICS AND TITLES

Second Year Students

Bernard Chascin (Empie)
Recovery Process/Smelt Dissolving Step
"Energy and Safety Improvement of the Kraft Recovery System through Smelt Solidification"

Denise Martin (Nichols)
Kraft Recovery Process/Char Combustion Gas Analysis
"Implementation of FTIR on the DOE Flow Reactor Measurement of CO_2 and CO above a Burning Char Bed"

Clint T. Seymour (Empie)
Recovery Systems
"The Application of the Direct Alkali Recovery System to the Kraft Pulping Process"

First Year Student

Matthew Casper (Horton)
Recovery Process/Furnace Modeling
"An Advanced Process Control Strategy for the Kraft Recovery Furnace"

A490

Ph.D. Theses In Progress

Student	*Passed A390*	*Subject*
Medvecz, Pat	*08/87*	***Spectroscopic Evaluation of the Gas Phase above a Burning Black Liquor Char Bed***
Verrill, Chris	*12/87*	***Chemical Fume Formation during Kraft Black Liquor Droplet Combustion***
Spielbauer, Tom	*07/88*	***Examination of the Mechanisms Controlling the Droplet Size Distribution of a Black Liquor Spray***
Lee, Stacy	*06/90*	***CO_2 Gasification of Black Liquor Char***
Thompson, Laura	*06/90*	***Formation of the Oxides of Nitrogen in Kraft Recovery Boilers***
Meyer, Dan	*08/90*	***Black Liquor Characterization by Near Infrared Spectroscopy***

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PERFORMANCE IMPROVEMENT OF THE KRAFT RECOVERY SYSTEM THROUGH SMELT SOLIDIFICATION	*Chascin (Empie)*	*72*
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AN EXAMINATION OF THE MECHANISMS CONTROLLING THE DROPLET SIZE DISTRIBUTION OF A SPRAY	*Spielbauer, et al.*	*123*
BLACK LIQUOR DELIVERY SYSTEMS (Project 3657-2 -- DOE Funded)	*Lien*	*136*

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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CHEMICAL RECOVERY

PROJECT ADVISORY COMMITTEE

Project 3473-1

FUNDAMENTAL PROCESSES IN ALKALI RECOVERY

December 14, 1990

PROJECT SUMMARY FORM

DATE: December 14, 1990

PROJECT NO. 3473-1: FUNDAMENTAL PROCESSES IN ALKALI RECOVERY

PROJECT LEADERS: H. Jeff Empie, Kenneth M. Nichols

IPST GOAL:

Increase capacity of existing systems.

OBJECTIVE:

A quantitative description of all key processes in the burning of kraft black liquor is to be developed, encompassing reaction paths and rate equations for drying, pyrolysis, gaseous combustion, char oxidation, sulfide formation and fume formation. The overall goal is a comprehensive understanding of black liquor combustion and application of that knowledge to improve recovery boiler performance.

CURRENT FISCAL YEAR BUDGET: $280,000

PRIOR RESULTS:

Char Gasification

The rate of gasification of a specific black liquor char with CO_2 was measured for a 5% CO_2 concentration in N_2. Twelve gasification tests were performed at four operating conditions, giving triplicate data for each condition. The four operating conditions were the four possible combinations of two gas flow rates (5 slpm, 10 slpm) and two temperatures (700°C and 800°C). The data were being analyzed.

Fume Formation

Results were limited, since the Ph.D. (Chris Verrill) student conducting this work was at James River Corporation's Corporate Research and Development facility doing an industrial internship not related to fume formation. The experimental equipment constructed in Appleton was being reassembled.

FT-IR Measurements

A detailed temperature profiling of the electrically heated cell was performed. Temperature gradients within the cell were found to be negligible. Results of temperature calculations from low temperature (25-500°C) spectra yielded accuracies of 1-3%. Results for higher temperatures (500-1000°C) were not as good due to complications with obtaining high quality CO absorption spectra, as well as an incomplete knowledge of the absorption of infrared radiation by CO at these high temperatures.

Work was initiated to install the FT-IR instrumentation on the DOE flow reactor for CO/CO_2 and temperature measurements during black liquor combustion. Design and selection of the optical arms which transmit the IR beam from the optical table to the reactor and from the reactor to the detector, and modifications to the view ports of the flow reactor were being examined.

SUMMARY OF RESULTS SINCE LAST REPORT:

Char Gasification

Analysis of the CO_2 char gasification rate data indicated kinetic control in the 700-800°C temperature range. This range needs to be extended to 1200°C as it is expected that mass transfer will become rate limiting at some intermediate temperature.

The char bed reactor, including the droplet generator and the in-flight reactor, have been reassembled and successfully tested. Modification of the char bed reactor to allow application of the FTIR required the fabrication of a new char retainer and a new gas jet. The gas jet was adjusted to obtain velocities close to those measured during previous testing.

Fume Formation

Design and construction of the experimental equipment has been completed. The performance of the reconstructed droplet combustion furnace was compared to that of the Appleton installation and found to perform satisfactorily over the specified operating conditions of 600-900°C and mean gas velocities of 1-5ft/s. Successful operation of the moving filter tape assembly and vacuum system has been demonstrated. Two test liquor samples have been obtained from Weyerhaeuser Company that represent high and low rates of fuming as observed in their mills.

FT-IR Measurements

Temperature measurements using the FT-IR instrument in the heated gas cell with N_2/CO mixtures were completed. Differences between temperature values measured by FT-IR and temperature values measured by the thermocouples are 3.2% or less in the range 25°C to 1000°C. and CO concentrations in the range 3% to 10% (volume). Absorption of CO decreases with increasing temperature, but was not found to depend on CO concentration. Presently, the specific relationship between absorption and temperature is being determined for each spectral line for temperatures up to 1000°C. These are the first data of this type that have been obtained anywhere at temperatures this high.

Implementation of FT-IR on the char bed reactor was accomplished. Hardware problems with the extended optics were remedied by the manufacturer. New support arms were built which provide stability to the extended optics. The extended optics and support arms were installed and aligned, and it was demonstrated that a FT-IR signal can be transmitted from source to detector. The table with extended optics installed was wheeled to the char bed reactor and back to Lab 360, demonstrating the movability of the equipment. New jacks have been installed on the table legs to provide increased flexibility in table height adjustment.

Smelt Solidification

A project looking at crystallization of molten smelt prior to its addition to the green liquor dissolving tank is under way. A lab scale fluidized bed crystallizer has been designed and fabricated to demonstrate feasibility of the concept. Potential process benefits for this process step include elimination of the potential for smelt-water explosions, improved energy recovery, reduced TRS emissions, elimination of the need for shatter jet steam, and improved control of green liquor concentration.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

Char Gasification

The rate of gasification of furnace representative kraft char will be pursued for temperatures ranging from 600-1200°C, including the threshold temperature where mass transfer becomes rate limiting. Ultimately, a rate expression will be developed for incorporation into the recovery furnace model. It is anticipated that a plug flow reactor of char particles will be used to experimentally determine the inherent reaction rates of $C_{(s)} + CO_2 \text{ ---> } 2CO$ for black liquor chars.

Char burning tests on the DOE reactor with the FT-IR in-place will be run to provide data on CO/CO_2 concentration and temperature in the gas phase immediately above the char bed.

Fume Formation

Experiments will be carried out to determine the time and duration of the fuming events occurring during black liquor droplet combustion by coordinating combustion progress (from video images) with the location of the fume on the filter tape. Mechanisms of fume formation will be hypothesized based on the experimental data.

FT-IR Measurements

The absorption data being determined for temperatures up to 1000°C will be used to predict CO concentrations from FT-IR spectra. Comparison will be made to other reported CO absorption data and to theoretically predicted results.

Smelt Solidification

The lab scale fluidized bed crystallizer will be run to establish feasibility of the process concept. Sensitivity of bed operation to temperature and feed rate will be examined.

STUDENT RESEARCH:

P. Miller, Ph.D.-1986; K. Goerg, M.S.-1986, Ph.D.-1989; K. Kulas, M.S.-1986, Ph.D.-1989; D. Sumnicht, M.S.-1986, Ph.D.-1989; G. Aiken, Ph.D.1987; C. Verrill, M.S.-1987, Ph.D.-1992; M. Robinson, Ph.D.-1987; F. Harper, Ph.D.-1989; G. Kulas, Ph.D.-1989; G. Maule, M.S.-1988; P. Medvecz, Ph.D.-1991; D. Miller, M.S.-1991; S. Lee, M.S.-1990, Ph.D.-1994; B. Chascin, M.S.-1991.

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Atlanta, Georgia

CHEMICAL RECOVERY

PROJECT ADVISORY COMMITTEE

Project 3671

A STUDY OF THE FEASIBILITY OF THERMAL DESTRUCTION OF CHLORINE-CONTAINING CONCENTRATED STREAMS FROM CLOSED CYCLE PROCESSES (NCASI FUNDED)

December 14, 1990

PROJECT SUMMARY FORM

DATE: December 14, 1990

PROJECT NO. 3671: A STUDY OF THE FEASIBILITY OF THERMAL DESTRUCTION OF CHLORINE-CONTAINING CONCENTRATED STREAMS FROM CLOSED CYCLE PROCESSES (NCASI FUNDED, part of the 301(m) Research and Development program)

PROJECT LEADER: Kenneth M. Nichols

IPST GOAL:

Part of overall IPST program goal to improve pulping and bleaching technology, with emphasis on environmental impact.

OBJECTIVE:

Evaluate potential technologies for thermal destruction of concentrated streams from closed cycle processes in a device other than a kraft recovery furnace.

CURRENT FISCAL YEAR BUDGET: $30,000 (Project completed)

PRIOR RESULTS:

Characterization of the Closed Cycle Streams

Necessary quantities of effluent from both the C/D first bleach stage and the first-stage caustic extraction were obtained. These samples were analyzed for total solids, total organics, organic chlorine (as AOX), elemental composition (C, H, O, S, Cl, Na, K), and heating value of the dried solids.

Two closed cycle treatment technologies were selected for the laboratory treatment of these bleach plant effluents: ultrafiltration and reverse osmosis. Laboratory-scale filtering equipment was leased from Niro Atomizer in Hudson, Wisconsin.

The unit was of a scale appropriate for research and development and could be used for both ultrafiltration and reverse osmosis. The average filtration capacity was approximately 35 liters of filtrate per hour.

Combustion Behavior of the Streams

Various experimental methods were considered for measuring the time-temperature destruction behavior of specific chemical compounds. These included TGA (Thermal Gravimetric Analysis), DSC (Differential Scanning Calorimetry), and a high-temperature tubular reactor for conducting gas-phase thermal decomposition studies of organic substances. This thermal reactor uses a counterflow heat exchanger in conjunction with a narrow-bore quartz tubular reactor to obtain precise control over physical factors, such as exposure temperature and mean residence time. Gaseous species are subjected to essentially a square-wave thermal pulse as they pass through the thermal reactor. This thermal reactor has been used by others to measure thermal decomposition profiles and kinetic data on nearly 100 different hazardous organic compounds.

SUMMARY OF RESULTS SINCE LAST REPORT:

Characterization of Closed Cycle Streams

Using laboratory-scale filtration equipment, samples were obtained of chlorine-containing concentrates from closed cycle processes. Four mill effluents were treated with ultrafiltration (UF) and with reverse osmosis (RO), giving eight samples of concentrated streams. Filtration flux rates, removal efficiencies, and concentrate solids levels were representative of values reported for previous laboratory and pilot scale ultrafiltration of bleach plant effluents.

The UF treatment was selective in removal efficiencies, yielding a higher level of organics in the concentrates compared to inorganics levels. This resulted in UF concentrates having higher levels of carbon, organic-to-inorganic ratio, and heating value, and lower levels of ash than RO concentrates, making the RO concentrates less desirable as a fuel. The compositions of UF concentrates were similar to black liquor solids, with the notable exception of higher chlorine levels. Heating values of UF concentrates were similar to or higher than heating values for black liquor solids. Molar ratios of Na to Cl showed an excess of Cl for concentrates of C/D effluents and an excess of Na for concentrates of E1 effluents.

Densities of the concentrated streams were dependent primarily on weight percent solids and temperature. A two-parameter equation can thus predict the density of the concentrated streams based on a knowledge of the solids and the temperature. The densities of the concentrated streams were found to be nearly identical to black liquor solids densities.

Viscosities correlated well with percent solids and temperature for individual streams, but varied dramatically among streams. Two streams, at similar levels of solids and temperature, yielded viscosities which differed by greater than a factor of ten. Thus, a single correlation cannot adequately describe viscosity for a variety of concentrated streams.

Combustion Behavior of the Streams

Isothermal mass loss data were obtained for two of the concentrates heated in air at 700 and 800°C for 5 to 600 seconds. These data show that the burning occurs by devolatilization and heterogeneous char oxidation. A two part model describes the mass loss data very well and shows that both devolatilization and char burning are approximately first order reactions with respect to concentration of combustibles. Data on the fate of chlorine show that as the concentrate is heated at 700 and 800°C, organic chlorine compounds are destroyed at a rate 2-5 times more rapid than the rate of total combustible matter destruction. The decrease in organic chlorine is mirrored by a commensurate increase in inorganic chlorine found in the ash residue which remains after heating. Thus, upon heating in air, the fate of the organic chlorine is to be trapped as NaCl in the inorganic solid phase. This is true as long as the concentrate contains a molar excess of sodium over chlorine. This is a significant result, implying that emissions of chlorinated organics (such as PCDD/PCDF) are minimized by the presence of excess alkali which traps the chlorine in the solid ash residue.

Definition of Process Concepts

Feasibility is high for thermal destruction of UF concentrates of E1 effluents, while it is much less for thermal destruction of other concentrates. Fluidized bed combustion is an attractive thermal destruction technology for these concentrates because it will provide for effective organics destruction at temperatures sufficiently low that the non-combustible ash will remain in the solid phase.

Since the chemical composition, heating value, and physical properties of UF concentrates are similar to kraft black liquor, it may be feasible to add these concentrates to black liquor and burn the mixture in a recovery furnace. The reasonably low levels of chlorine in concentrate solids (8-9 weight %) may not result in chloride levels in the recovery cycle which are higher than levels experienced routinely at coastal mills.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

A Phase II research proposal to NCASI is being written for work to be directed along two parallel paths: potential for fluid bed combustion of concentrates, and potential for burning of concentrates in recovery boilers.

Fluidized bed combustion should be tested in a laboratory-scale or small pilot-scale fluidized bed combustor where conditions of temperature, gas residence time, solids residence time, stoichiometry, and other key variables can be controlled and manipulated. Such tests should demonstrate the temperatures and residence times necessary to accomplish high levels of destruction of organics as well as high levels of chlorine trapping as NaCl. The emissions of HCl and of PCDD/PCDF and other chlorinated organics would be measured to assess the potential for emission of these compounds.

Since the chemical composition, heating value, and physical properties of concentrates are similar to kraft black liquor, destroying concentrates by adding them to black liquor and burning them in a recovery furnace may be accomplished without derating the fuel value. That the levels of chlorine in concentrate solids (8-9 weight %) may not result in recovery cycle chloride levels higher than levels experienced routinely at coastal mills would have to be demonstrated.

PROJECT SUMMARY FORM

DATE: December 14, 1990

PROJECT NO. 3605: KRAFT RECOVERY FURNACE MODELING CAPABILITY

PROJECT LEADERS: H. Jeff Empie, Robert R. Horton, Kenneth M. Nichols

IPST GOAL:

Increase the energy efficiency and productivity of recovery boilers.

OBJECTIVE:

Develop a comprehensive mathematical modeling capability for the fireside processes in a recovery furnace. The model is to be based on first principles, will incorporate and integrate the results of ongoing fundamental studies of black liquor combustion, and will be validated with actual operating data.

CURRENT FISCAL YEAR BUDGET (JULY 1990 TO JUNE 1991): $225,000 - IPST
$412,500 - DOE
$ 48,800 - API

PRIOR RESULTS:

Simulations with the recovery furnace model provided extraordinary insight into the nature of the black liquor combustion process. The model showed that the main mode of combustion is particle burning. Carryover is not simply determined by liquor spray size, but rather by a complex relationship between drop size, gas flow patterns, and oxygen concentrations. Gas flow patterns are determined primarily by the air inlet geometry and are not greatly modified by liquor sprays and in-flight combustion. Bed shape can have a strong effect on gas flow patterns. Unfortunately, full convergence of the computations was not achieved, as judged by the non-convergence of carryover values. For the model to be useful as a tool for recovery boiler operational improvement, it was concluded that computation time had to be significantly reduced, while at the same time, certain model assumptions had to be relaxed.

SUMMARY OF RESULTS SINCE LAST REPORT:

A four-year program to develop a validated recovery boiler modeling capability was started on September 30, 1990 and will feature close cooperation between IPST, W.J. Frederick at Abo Akademie in Finland, the University of British Columbia (UBC) in Vancouver, and T.M. Grace in Appleton. Funding will be shared by IPST (33%), the Department of Energy ($60%), and the API Recovery Boiler Committee (7%).

Full realization of the modeling capability will require the development of a new state-of-the-art computational fluid dynamics code employing multi-gridding techniques that is specifically adapted to the needs of a recovery boiler model. The development of this code is being carried out by the group at UBC. Jim Frederick will be responsible for refining the single particle combustion model and modeling sulfur release and capture phenomena. He will also provide access to the laboratory facilities, equipment, personnel, and collaborative research results of the Combustion Chemistry Group at Abo Akademie. Tom Grace will serve as an eminently qualified technical consultant with years of recovery technology experience, both in operations and with modeling. The API Recovery Boiler Committee R & D Subcommittee will monitor progress and insure rapid utilization of the results of the modeling work. An IBM RISC 6000 computer workstation is to be purchased, providing a computational speed-up of greater than one order of magnitude.

Supporting experimental studies, in addition to those at Abo Akademie, include the kinetics of char gasification, characterization of fume deposition phenomena under experimental conditions representative of an operating recovery boiler, the influence of bed shape on furnace gas flow patterns and therefore particle entrainment, and measurement of actual furnace gas velocities and temperatures in an operating recovery boiler to validate the model.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

Year one will see development of: a single particle combustion model; a furnace combustion model with fixed velocity, temperature, and concentration fields; a computational fluid dynamics code for a 2-dimensional gas jet interaction with crossflow; laboratory equipment to determine the kinetics of kraft char gasification; fume formation rate data enabling formulation of the mechanism of formation; and a furnace diagnostics prototype for obtaining furnace model validation data.

STUDENT RESEARCH:

A. Jones, Ph.D.-1988, A. Walsh, Ph.D.-1988, D. Sumnicht, Ph.D.-1989, T. Kindler, M.S.-1990.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL RECOVERY

PROJECT ADVISORY COMMITTEE

Project 3657-2

KRAFT BLACK LIQUOR DELIVERY SYSTEMS

December 14, 1990

PROJECT SUMMARY FORM

DATE: December 14, 1990

PROJECT NO. 3657-2: KRAFT BLACK LIQUOR DELIVERY SYSTEMS
(Supported by the Office of Industrial Programs -
U. S. Department of Energy)

PROJECT LEADERS: Terry N. Adams, H. Jeff Empie

IPST GOAL:

Increase recovery boiler throughput and operating efficiency through improved liquor spraying technology at modest capital cost.

OBJECTIVE:

Develop new and improved black liquor spraying nozzles by understanding the characteristics of spray behavior and reducing the fraction of undersize droplets to avoid carryover and pluggage and to accommodate firing higher solids liquors.

CURRENT FISCAL YEAR BUDGET: $300,000

PRIOR RESULTS:

Analysis of spraying data led to a number of conclusions about droplet formation mechanism, nozzle flow/pressure drop characteristics, fluid sheet thickness, and drop size distribution of black liquor sprays. Considerations of the observed mechanism of droplet formation suggested a major revision was needed in the theory of how droplets form from splashplate and similar nozzles. The standard deviation about the median droplet size for black liquor was nearly the same as for a wide variety of other fluids and nozzle types. Preliminary correlations for fluid sheet thickness on the plate of a splashplate nozzle for black liquor showed strong similarities to other fluids. The flow/ΔP characteristics of black liquor nozzles followed a simple two-term relationship similar to other flow devices. In routine mill operation only the fluid acceleration in the nozzle was important; viscous loses were quite small.

The Flash X-ray (FXR) shadowgraph technique originally proposed for this program was shown to be inferior to use of a high-speed video approach with respect to image contrast. In addition, the number of FXR images per run was limited so that droplet history could not be recorded; such is not the case with the video approach.

SUMMARY OF RESULTS SINCE LAST REPORT:

Assembly of the black liquor spray system has been completed, including installation of the spray tank, viscosity meter, all of the piping, waste liquor storage tanks, a gas scrubber system, and all of the electrical sensor and control wiring. A data acquisition system has also been connected so that information on liquor conditions is automatically recorded.

Windows on the front and back of the tank have been installed to allow the spray pattern to be video-taped. Lights and a translucent plexiglass screen are used to back-light the droplets. The high speed video-camera has been tested and appears to provide an adequate recording for the image analyzer, even with water. Black liquor produces an excellent high contrast image.

A series of spray tests was performed using black liquor from the Mead mill in Phenix City, Alabama. Two different nozzles were tested, a B+W 15/52 splash-plate and a CE V-jet. The nozzles were tested at solids levels ranging from 50 to 65%, viscosities from 33 to 270 cP, temperatures from 77 to 110°C, and flow-rates of 15 and 25 gpm.

Analysis of the data acquisition files has been completed and all of the sensors including the viscometer appear to be working well. A correlation was developed to calculate the viscosity from the temperature and % solids for this black liquor.

Video images were recorded at six positions in the spray pattern for each test condition. A review of these high speed images showed that in six of the seventeen tests the liquor was almost entirely in the form of drops. For the remaining tests some of the liquor was in long strands and drops connected by strands.

There are still two issues to be resolved before droplet analysis is possible: completeness of droplet break-up; and out-of-focus droplets. Because of the width of the spray pattern, the depth of field has been too narrow to capture all of the drops in focus. The depth of field can be improved by reducing the aperture, but because of the requirement for a fast shutter speed, it has been necessary to increase the light intensity to the tank. The video data have also indicated that the droplet formation process is not completed within the length of the spray tank for all tests conditions. This is especially true for the larger nozzles and at high viscosities. The length required for the drops to coalesce can be reduced by using smaller nozzles.

On July 10-14, 1989 a series of trials were conducted at James River's Camas mill to study blackliquor sprays in a recovery furnace environment. This project was a joint effort between the Institute of Paper Science and Technology and James River. High speed video images of sprays were taken through a gun port on Camas #4 Recovery Boiler. Each of three different nozzles was operated at two levels of liquor flow and fired liquor temperature. The major conclusions from analysis of furnace response data and high speed video images of the sprays are:

1. Changing one nozzle and/or firing conditions for a short period of time did not produce significant changes in furnace operation as indicated by particulate count or lower furnace temperatures.

2. Bed height was affected by transitory changes in fired liquor temperature and nozzle flow rate (pressure).

3. There is evidence of liquor sheet break-up by perforation which agrees with the findings in the IPST spray booth. There was not a lot of evidence of wave fronts and associated break-up in the liquor sprays studied.

4. Differences in break-up between nozzles were seen in the video images; however, it was not possible to detect variation due to firing conditions.

5. The video images were too optically dense to determine droplet size distribution by image analysis.

6. The video equipment may prove to be a valuable industrial tool for rapid evaluation of nozzle performance in the field and for optimization of firing conditions.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

Acquire additional nozzles from recovery boiler manufacturers and test in the IPST spray chamber. The characteristic nozzle dimension should be about 3/8 inch (e.g. #12 B&W nozzle). The small swirl cone nozzle we presently have is about this size.

Any future mill trials should carefully monitor bed response to operational changes to determine the time required for combustion to stabilize after each process change.

OVERHEADS/HANDOUTS

CHEMICAL RECOVERY GROUP - PERSONNEL

Jeff Empie - Group Leader, Professor

Ken Nichols - Assistant Professor

Bob Horton - Assistant Professor

Steve Lien - Assistant Scientist

Don Sachs - Sr. Technician

Doug Samuels - Sr. Technician

Chemical Recovery Group - Projects

DOE Funded:		*Annual Budget ($K)*
3657-2	*Black Liquor Delivery Systems*	*300*
3605-2	*Validated Recovery Boiler Modeling*	*550*
Dues Funded:		
3605-1	*Validated Recovery Boiler Modeling*	*300*
3473-1	*Fundamental Processes in Alkali Recovery*	*280*
A190		
A490	*FT-IR Measurements for Combustion Diagnostics*	
A490	*Fume Formation*	
A490	*Char Gasification*	
A490	*NO_x Formation in Recovery Boilers*	
A490	*On-line Analysis of Black Liquor by NIR Spectroscopy*	
A490	*Black Liquor Droplet Formation Mechanims*	
A190	*Smelt Solidification*	
A190	*Direct Alkali Recovery (Kraft)*	
A190	*Advanced Control System for the Recovery Boiler*	
NCASI Funded:		
3671	*Incineration of Chlorine-Containing Concentrated Mill Streams*	*75*

FT-IR MEASUREMENTS IN A BLACK LIQUOR COMBUSTION ENVIRONMENT

Pat Medvecz

Ken Nichols, Faculty Advisor

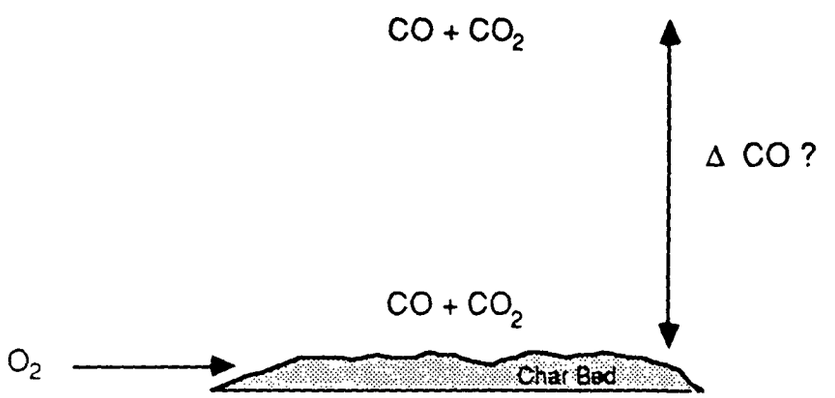
Project Origins/Motivation (1987) - Dave Clay

- Spectroscopic Techniques Extensively Used In Other Combustion Systems
- Application To Black Liquor Combustion
  - Explore Unknown Elements Of Combustion
  - *In Situ* Measurements
  - Applicable To Large Range Of Problems
  - Char Combustion; CO/CO_2

FT-IR Absorption Spectroscopy In Combustion

- All Major Combustion Species Detectable (Except Homonuclear Diatomic Molecules)
- Yields Quantitative And Qualitative Concentration Information
- Gas Phase Temperatures Can Be Determined
- Used In Two Previous Combustion Studies

Char Combustion



Thesis Objectives

- Quantify, In A Black Liquor Combustion Environment
    - Carbon Monoxide
    - Carbon Dioxide
    - Gas Phase Temperatures
- Develop FT-IR Methods To The Point Where It Is A Useful Combustion Diagnostic Tool

Experimental Approach

- Design And Construct Char Burning Reactor
    - Facilitate The Combustion Of a Black Liquor Char Bed
    - Optical Accessibility To The Gas Phase
- Use Reactor To Evaluate Spectrometers
- Select, Purchase, And Set-Up Optical Equipment

Experimental Approach (Continued)

- Design And Construct High Temperature, 1000°C, Gas Cell
- Use Of Cell
  - Under Controlled Conditions, Learn To Make Temperature And Concentration Measurements
  - Determine The Limits Of Accuracy Expected From Spectroscopic Technique
- Evaluate Gas Phase Of Char Bed Reactor For CO And CO_2 Concentrations And Gas Phase Temperatures

Temperature Calculations, Herzberg

$$I_{abs} = |m| \cdot F(m) \cdot \nu \cdot \exp(-E(m)/k \cdot T)$$

I_{abs} = Intensity Of A Single Absorption Line
m = Index Of The Transition
ν = Frequency Of Transition
F(m) = Herman-Wallis Factor (Accounts For Vib-Rot Interactions)
E(m) = Rotational Energy Of Initial State Of The Transition
k = Boltzman Constant
T = Temperature

Temperature Calculations (Continued)

- Rearrange Herzberg Equation

$$\mathrm{Ln}(I_{abs}/|m|\cdot F(m)\cdot\nu) = E(m)/k\cdot(-1/T)$$

- Intensity Term: $\mathrm{Ln}(I_{abs}/|m|\cdot F(m)\cdot\nu)$
- Energy Term: E(m)/k)
- Plot Intensity Term Vs. Energy Term
- Slope Is Equal To -1/T

Concentration Measurements

- Beer's Law

$$I/I_o = e^{-\alpha cL}$$

- Lorentzian Line Shape

$$\alpha(\nu) = S(m) \cdot \gamma / [\pi \cdot ((\nu - \nu_o)^2 + \gamma^2)]$$

I/I_o = Transmission Of Sample
α = Absorption Coefficient
c = Gas Concentration
L = Path Length
S(m) = Line Strength
γ = Line Half-Width
ν_o = Frequency At Line Center

Concentration Measurements (Continued)

- Solve For Absorption Intensity

$$A(\nu) = \ln(I/I_o)/2.303 = \gamma \bullet L \bullet S(\nu) \bullet \gamma/[\pi \bullet ((\nu-\nu_o)^2 + \gamma^2) \bullet 2.303]$$

- Solve For Absorption Intensity At Peak Center

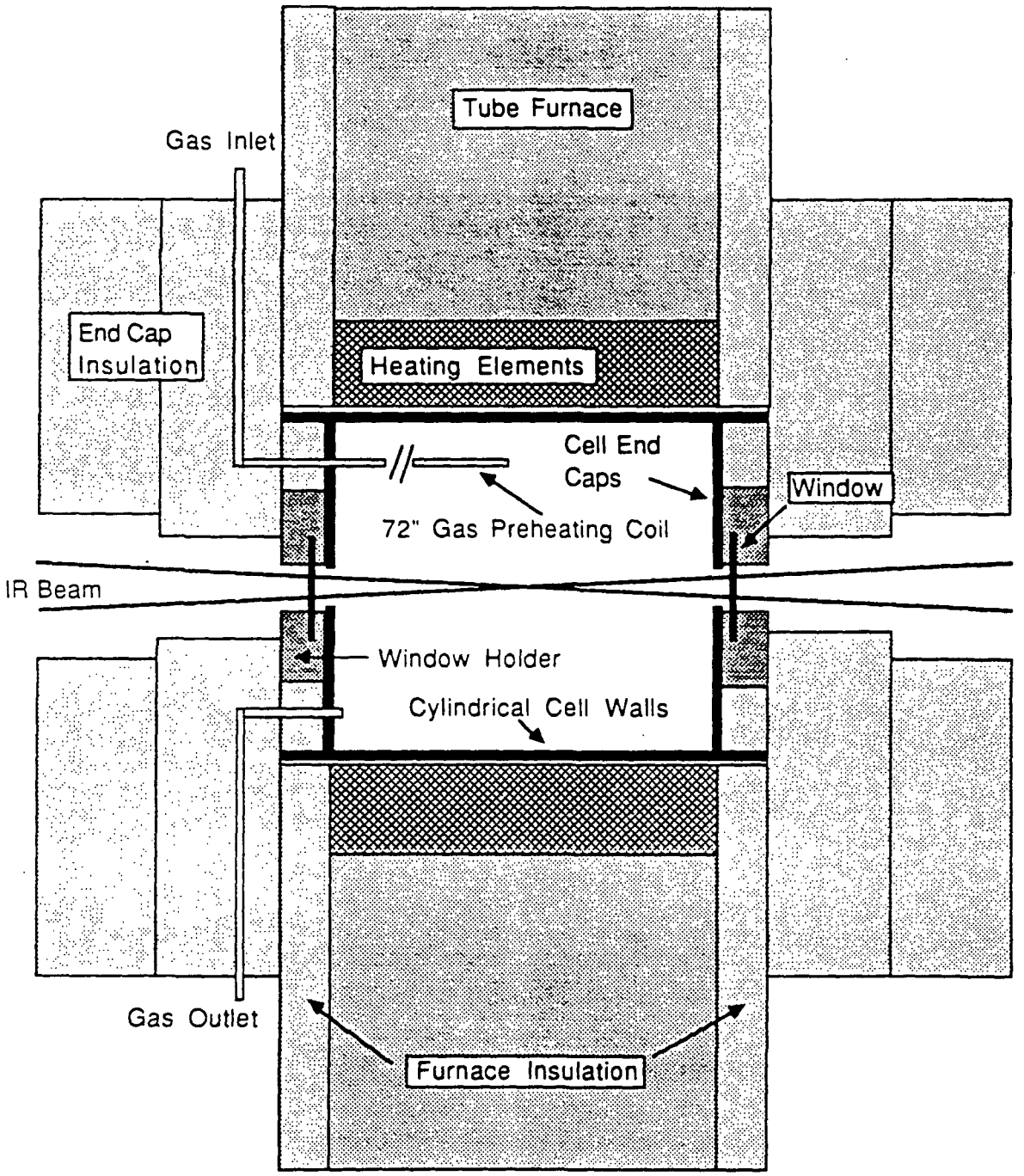
$$A(\nu_o) = c \bullet L \bullet S(m)/(\pi \bullet \gamma \bullet 2.303)$$

Complications To Theoretical Approach

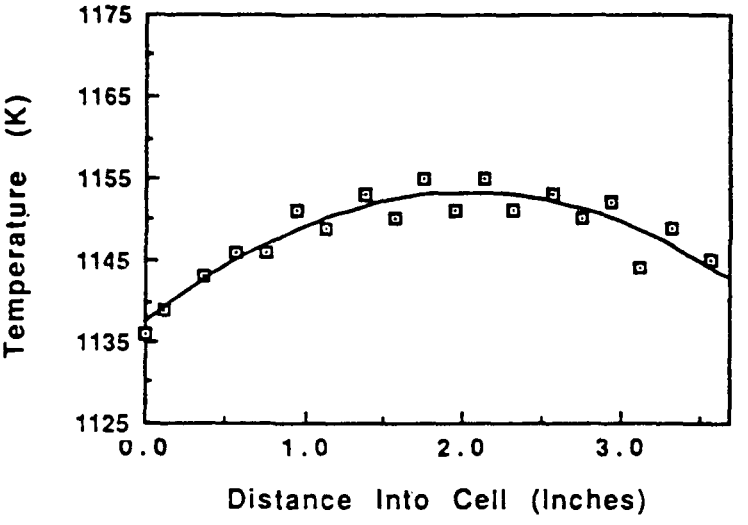
- Photometric Error
- Lack of Accurate Half-Width Data
- Lack of Line Strength Data

Results

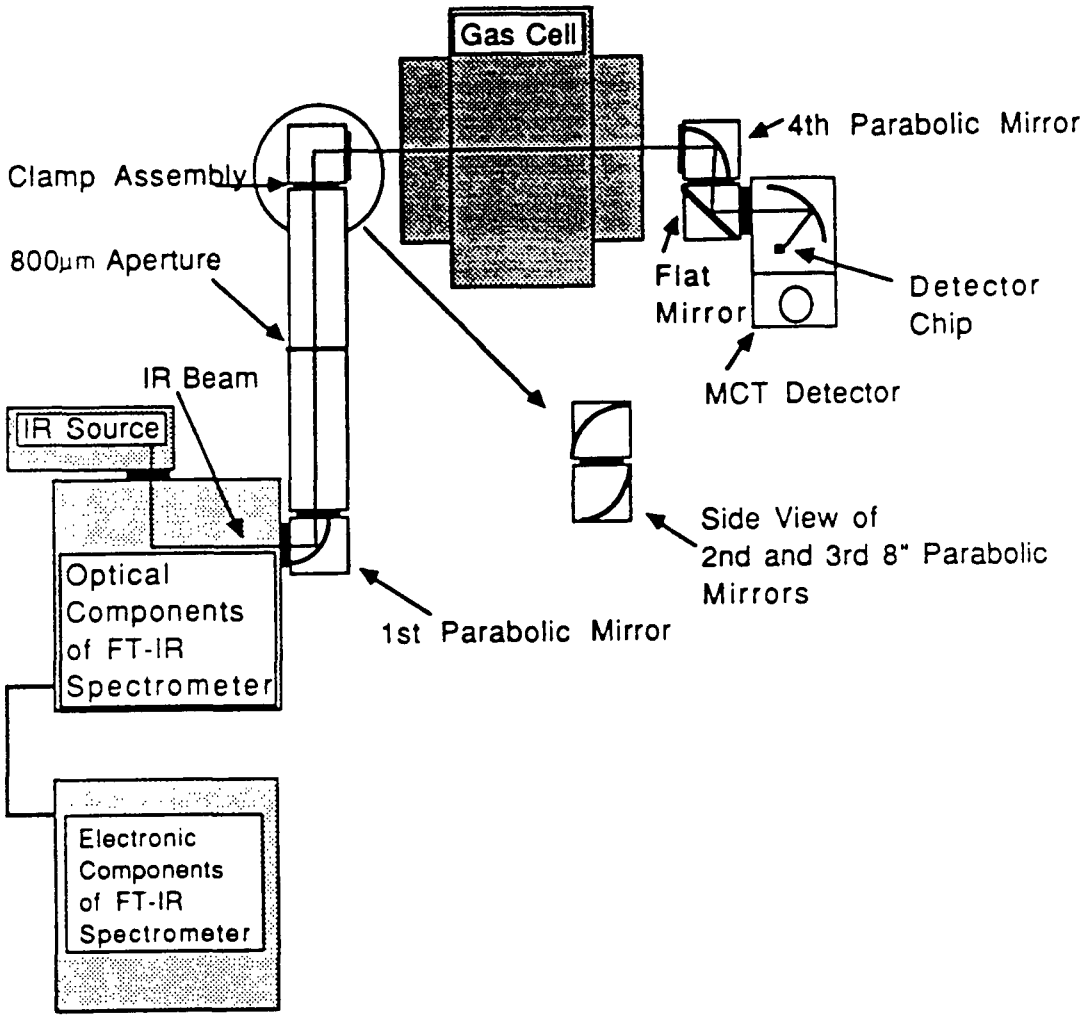
- Temperature Measurements
- Concentration Measurements
- DOE Reactor Trial



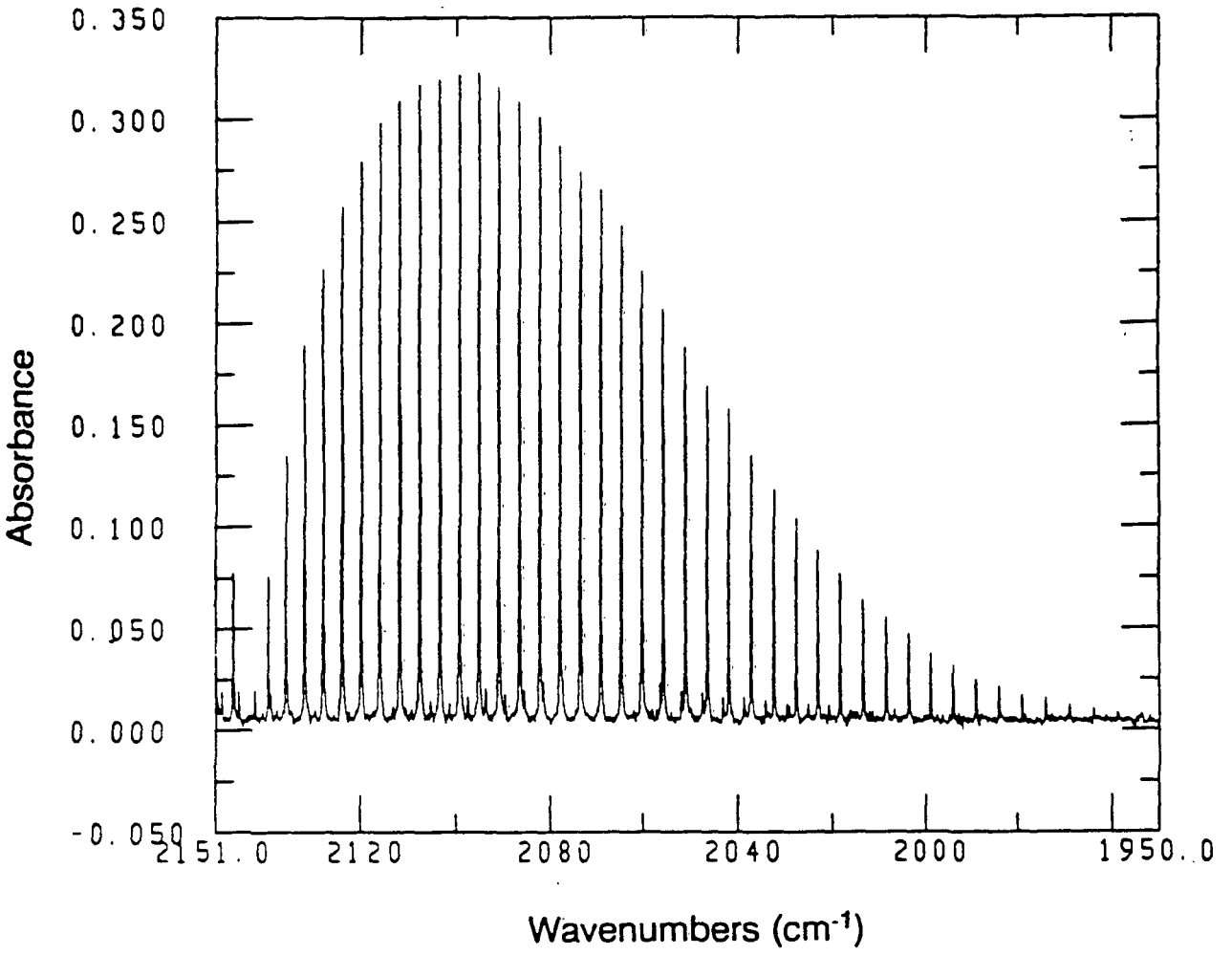
Schematic diagram of high temperature gas cell, tube furnace, heating elements, end cap insulation, and the path of the infrared beam.



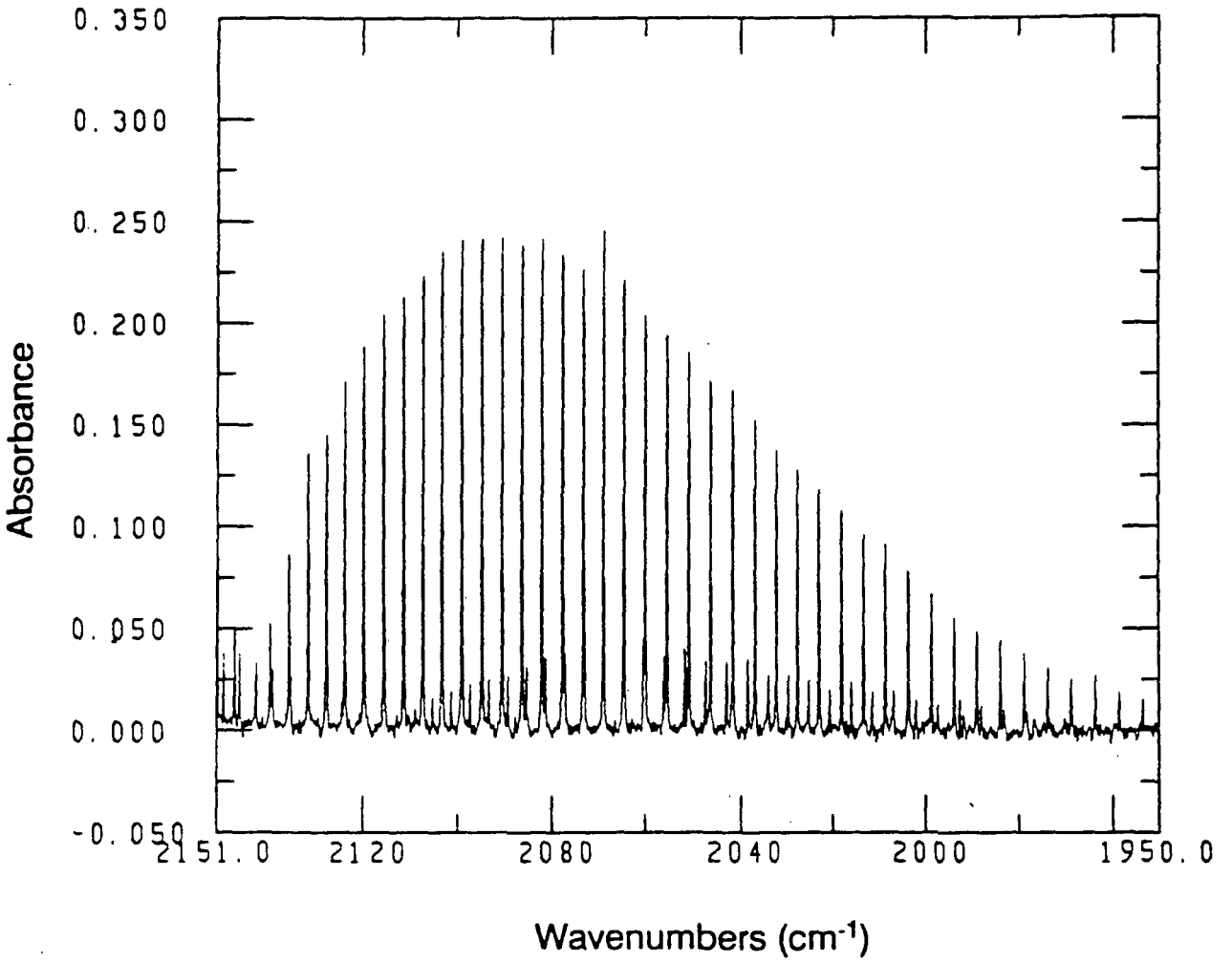
Gas temperature profile within the gas cell at a furnace set-point temperature of 1173 K.



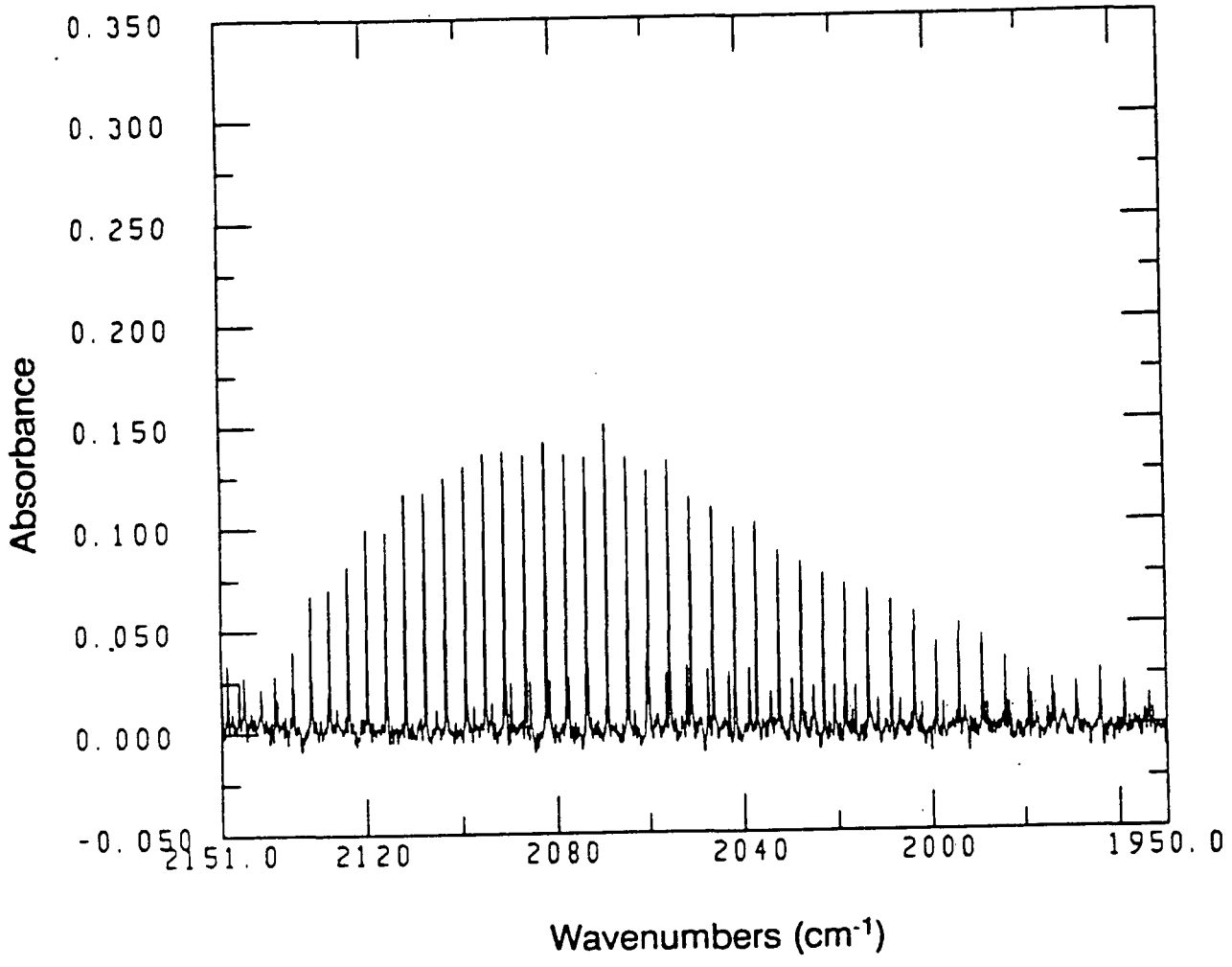
Overhead diagram of optical configuration including the FT-IR, Optibus components, high temperature gas cell, and MCT detector.



CO Absorption Spectrum At 746 K



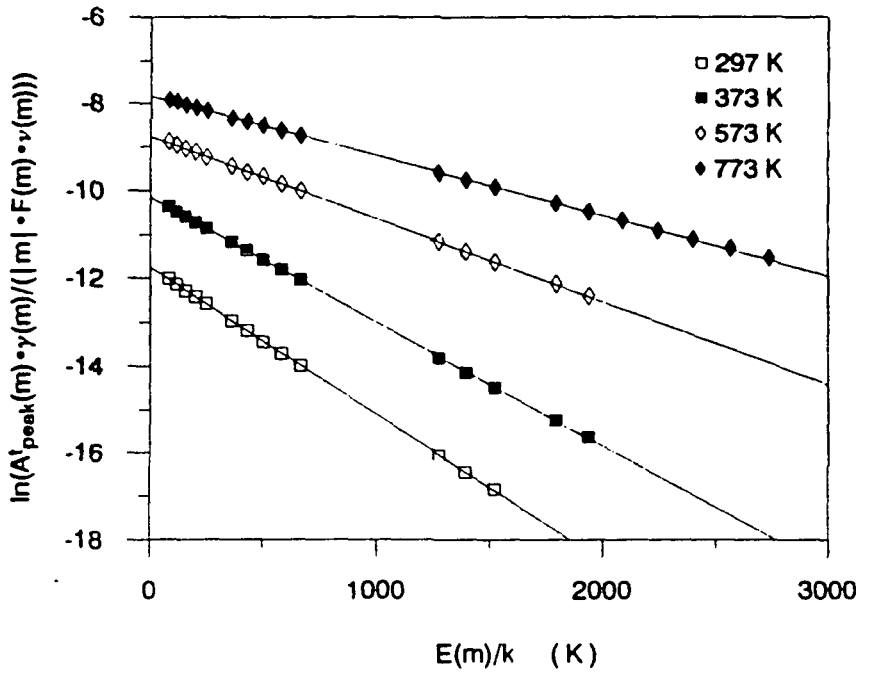
CO Absorption Spectrum At 1048 K



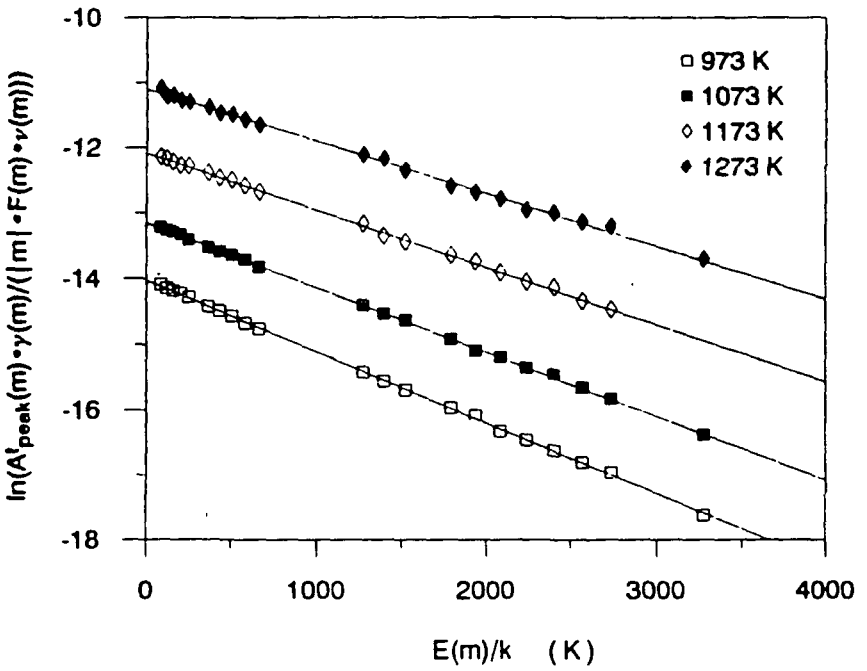
CO Absorption Spectrum at 1251 K

Results of Temperature Calculations from CO Absorption Spectra.

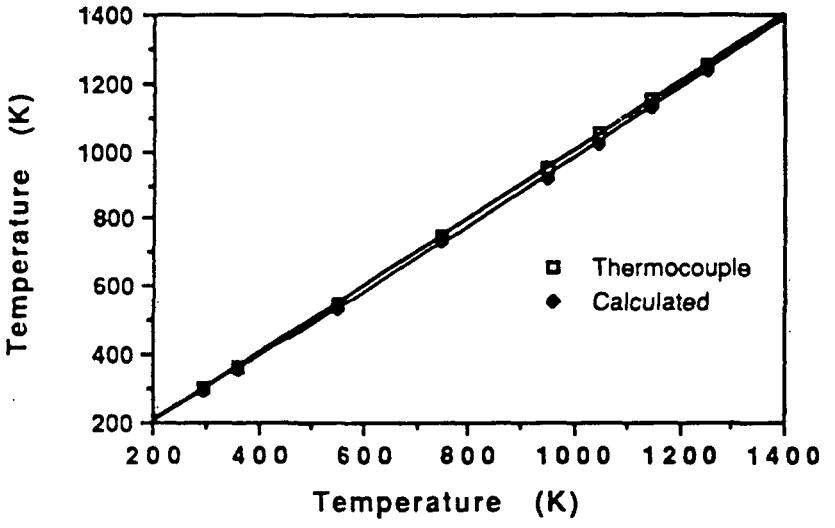
Furnace Set Point	Number of Spectra	Average Thermocouple Temp.	Average Calc. Temp.	Average Absolute Difference	Percentage Absolute Difference	Low	High	σ,(K)
297 K	9	297 K	296 K	1.6 K	0.5%	294 K	298 K	1.5
373 K	6	361 K	352 K	9 K	2.6%	349 K	353 K	1.4
573 K	6	547 K	533 K	14 K	2.6%	530 K	537 K	2.9
773 K	6	746 K	731 K	15 K	2.0%	727 K	735 K	3.7
973 K	6	948 K	917 K	31 K	3.2%	912 K	921 K	3.6
1073 K	6	1048 K	1021 K	27 K	2.5%	1020 K	1024 K	1.7
1173 K	6	1149 K	1132 K	17 K	1.5%	1117 K	1146 K	9.5
1273 K	12	1251 K	1234 K	21 K	1.7%	1202 K	1267 K	20.3



$Ln(A^{t}_{peak}(m) \bullet \gamma(m)/(|m| \bullet F(m) \bullet \nu(m)))$ vs. E(m)/k for representative spectra recorded at furnace set-point temperatures of 297, 373, 573, and 773 K.



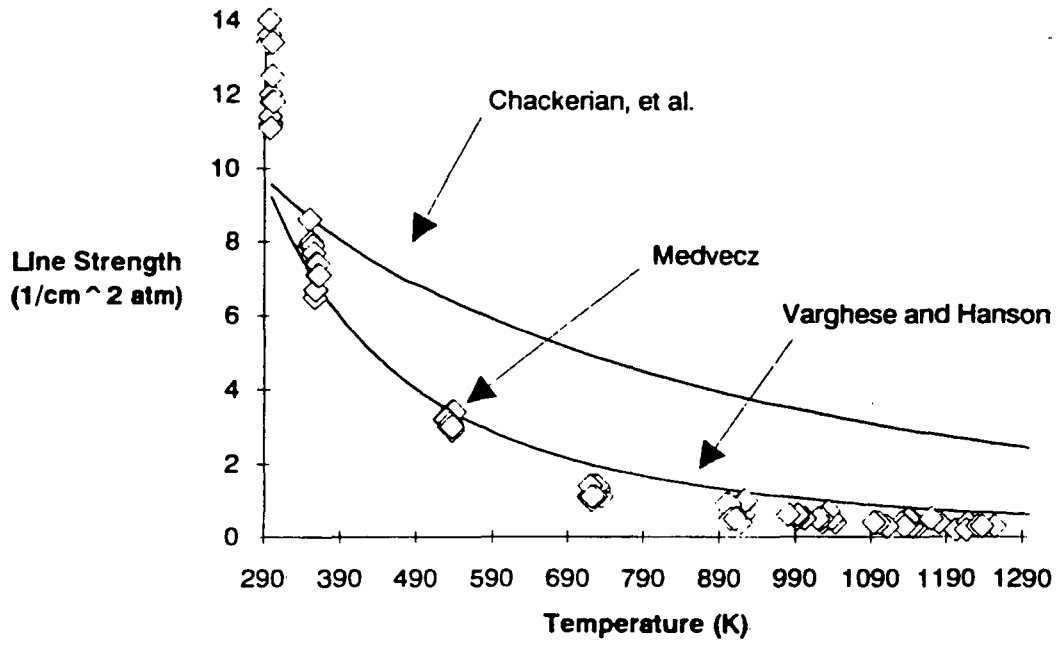
$Ln(A^t_{peak}(m) \bullet \gamma(m)/(|m| \bullet F(m) \bullet \nu(m)))$ vs. E(m)/k for representative spectra recorded at furnace set-point temperatures of 973, 1073, 1173, and 1273K



Plot of gas temperatures measured by a thermocouple compared to gas temperatures calculated from CO absorption spectra.

Results Of Concentration Measurements

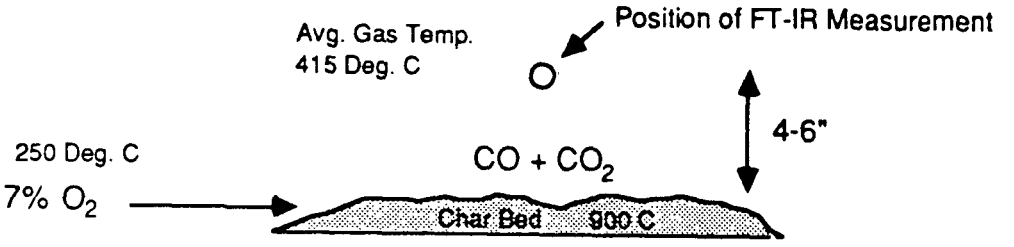
- Efforts Focused On Experimental Line Strength Measurements

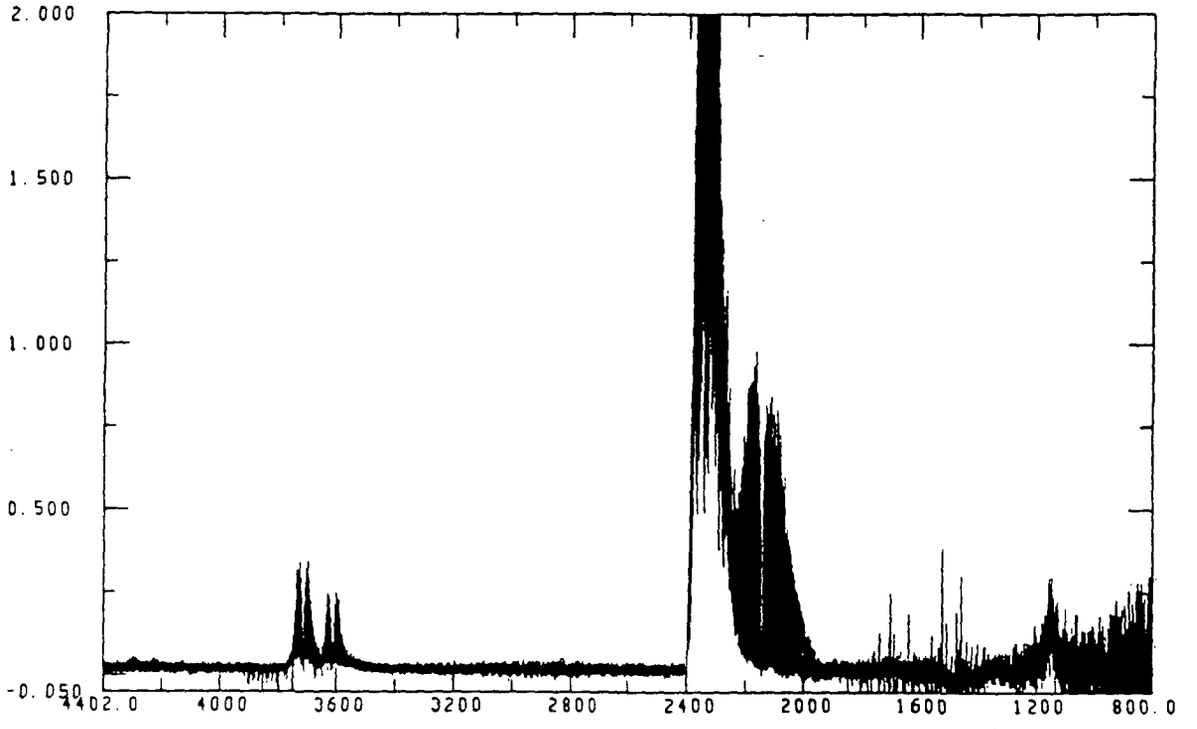

Line Strength
(1/cm ^ 2 atm)
14
12
10
8
6
4
2
0
Chackerian, et al.
Medvecz
Varghese and Hanson
290
390
490
590
690
790
890
990
1090
1190
1290
Temperature (K)

DOE Reactor Trial (Denise Martin, A190)

- Determine Feasibility Of Recording Absorption Spectra In The DOE Reactor

FT-IR Measurements In DOE Reactor




2.000
1.500
1.000
0.500
-0.050
4402.0
4000
3600
3200
2800
2400
2000
1600
1200
800.0

Future Work

- Complete Concentration Analysis In Gas Cell
- Measure CO And CO_2 Gas Concentrations And Gas Phase Temperatures In Combustion Environment
- Perform Additional DOE Trials

CHEMICAL FUME FORMATION DURING KRAFT BLACK LIQUOR DROPLET COMBUSTION

CHRISTOPHER L. VERRILL
A-490 THESIS

IPST

December 14, 1990

WHAT IS FUME?

Appearance:	1-10 μm smooth, white spheres
Composition:	Na_2SO_4, Na_2CO_3, and NaCl
Importance:	10-20% of liquor inorganics become fume.
Formation:	Vaporization of sodium, followed by condensation in gas stream as particulate.

DETRIMENTAL EFFECTS OF FUME

Fouls boiler tubes (efficiency, pluggage, corrosion)

Sootblowing requires >3% of process steam

Recycled inorganics lower HHV of liquor.

BENEFICIAL EFFECT OF FUME

Effectively captures sulfur gases, reducing emissions.

THESIS MOTIVATION

Higher solids firing will increase combustion temperatures and create increased amounts of fume.

Industrial studies confounded by simultaneous processes occurring in furnace.

Laboratory work limited to molten salt systems, results are only applicable to specific areas of furnace.

Only one known study of fuming from single droplets.

Predictive equations are needed for RFM.

INDUSTRIAL FUME STUDIES

Three types of particulates were found:

- Submicron-sized, smooth, spheres (major fraction)
- 2-10 μm pebbled, spheres (agglomerates)
- 2-3 mm shells and char fragments (<5% pptr dust).

Particulate loading a function of bed temperature.

INDUSTRIAL FUME STUDIES

Fume mostly Na_2SO_4 and Na_2CO_3 with some Na_2S, NaCl, and potassium analogues.

Little or no NaOH found in particulate.

Sulfate/Carbonate ratio increases with height.

Pptr dust mostly Na_2SO_4 with about 10% Na_2CO_3.

STAGES OF KBL DROPLET COMBUSTION

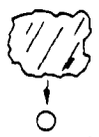
Drying

Water is evaporated
Temperature is kept down
Relatively slow process.

Volatiles Burning

Pyrolysis and gaseous combustion
Visible yellow flame
Volume expansion (swelling)
Relatively fast process.

Char Combustion



Burning on solid char surface
No apparent flame
Slow process, controlled by air supply.

Inorganic Reactions

After char collapse
Occasional sparks and visible fume cloud
Relatively slow process.

LABORATORY DROPLET FUME STUDIES

IPC Char Burning studies:

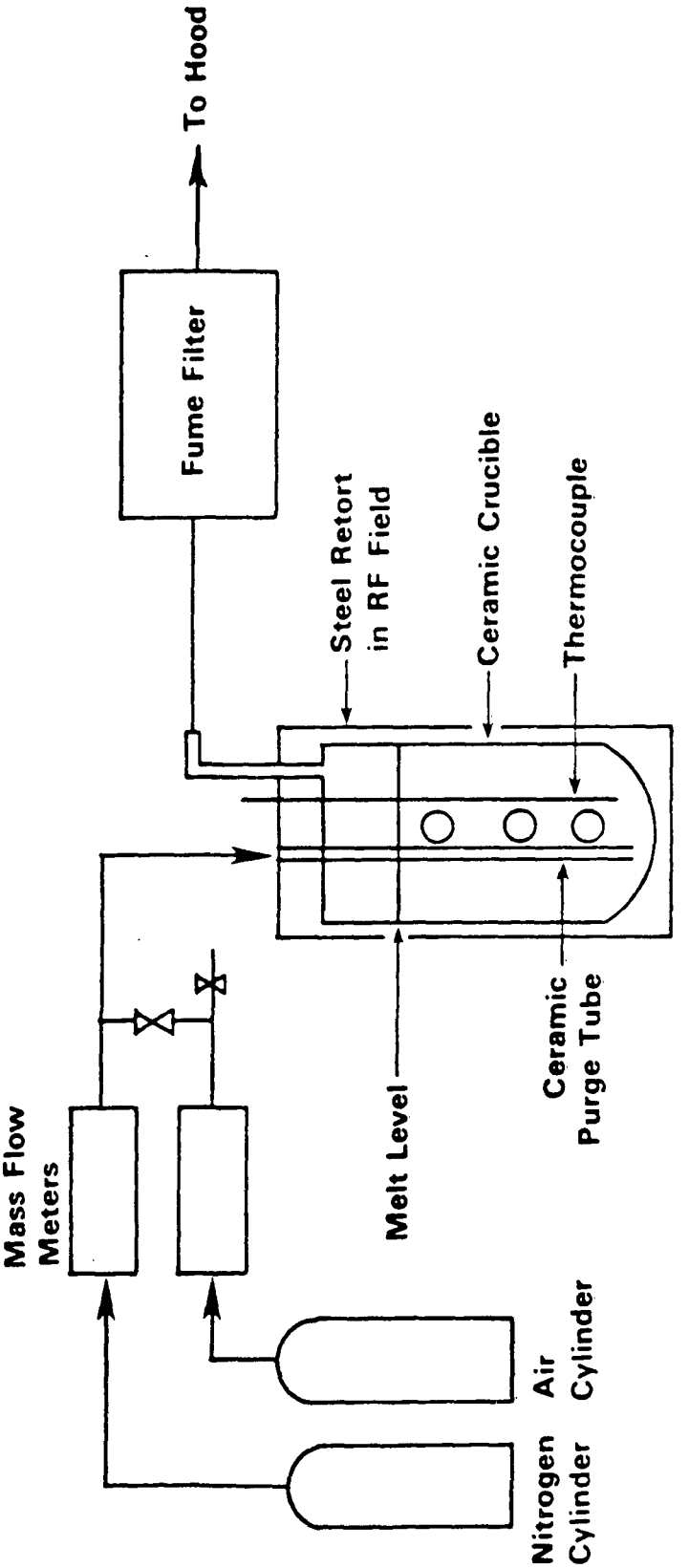
- Fuming increased with O_2 partial pressure
- C in char or CO_2 in gas did not suppress fuming.

LABORATORY DROPLET FUME STUDIES

Volkov and coworkers:

- Continuous Na loss throughout droplet combustion.
- Rate increases with increasing temperature and decreasing droplet diameter.

LABORATORY SMELT POOL REACTOR



LABORATORY SMELT POOL FUME STUDIES

Most intense fuming occurs under oxidizing conditions.

No effect of melt composition as long as Na_2S present.

Process not controlled by equilibrium thermodynamics, gas phase enhanced rate of sodium vaporization.

PROBLEMS WITH EQUILIBRIUM MODELS

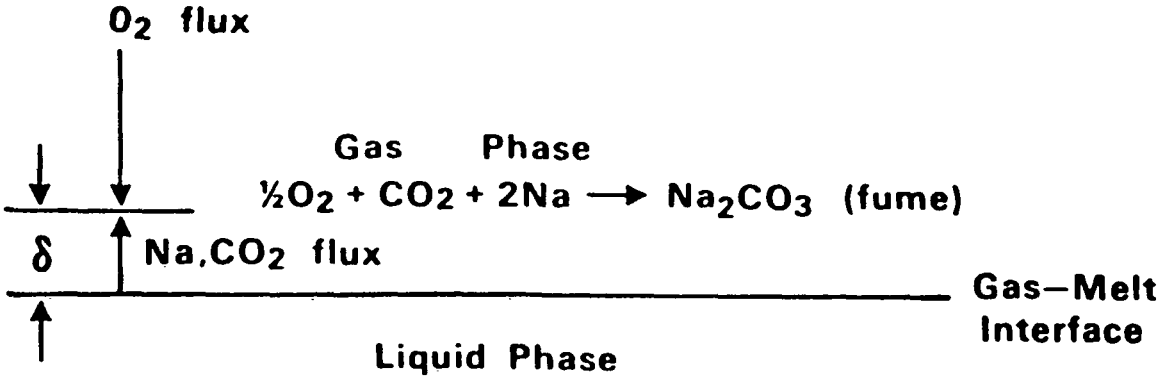
Predict order of magnitude of fume formed.

Good estimates of smelt composition.

Overpredict temperature dependance of fuming rate.

Predict presence of KOH and NaOH, not observed in fume.

FUME GENERATION UNDER OXIDIZING CONDITIONS



$$Na_2CO_3 + \tfrac{1}{4}Na_2S \rightleftharpoons \tfrac{1}{4}Na_2SO_4 + CO_2 + 2Na$$

THESIS OBJECTIVES

Build equipment for studying fume formation during droplet combustion.

Identify stage(s) of combustion when fume is formed.

Determine effects of combustion conditions, liquor composition, droplet size on fuming.

Develop model based on fundamental understanding and response to variation in combustion conditions.

EXPERIMENTAL APPROACH

Monitor droplet combustion progress with reaction time.

Understand reactor dynamics.

Detect amount of fume created during the course of combustion.

EXPERIMENTAL APPROACH

Manipulate process variables:

- Droplet diameter
- Liquor composition
- Gas temperature
- Gas composition
- Gas flow rate

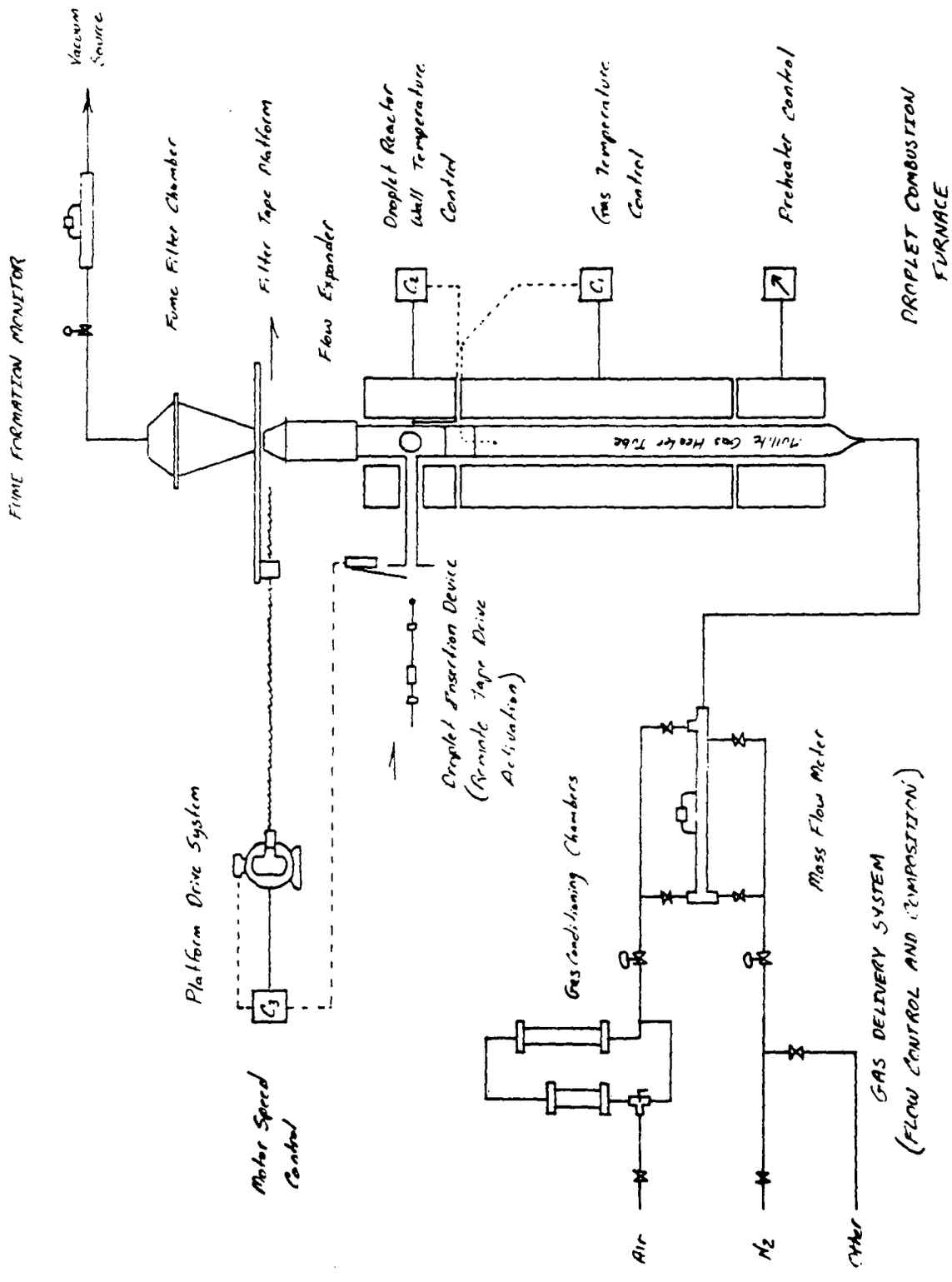
Measure fume mass accurately.

WORK COMPLETED

Apparatus assembled and tested.

Droplets burned to test fume filter mechanism.

SCHEMATIC OF EXPERIMENTAL SYSTEM



FURNACE PERFORMANCE

Temperature Range:	600-900°C	(112-1652°F)
Avg Gas Velocity:	1-5 ft/s	(30.5-152 cm/s)
Flow Rate:	0.51-3.41 scfm	(14.4-96.6 slpm)
Gas Concentration:	5-10% O_2 in N_2	

WORK REQUIRED TO COMPLETE THESIS

Develop lab technique of measuring amount of fume deposited on filter sections.

Study fuming events at various combinations of liquor, temperature, O_2 partial pressure, and flow rate.

Determine controlling factors for major fuming events.

Develop model of fuming event(s) and check validity.

INITIAL EXPERIMENTAL PLAN

1. Determine combustion time
2. Burn droplets - capture fume
3. Cut filter tapes in 9 sections
4. Measure concentration of Na & K by ICP
5. Measure concentration of CO_3, SO_4, Cl by IC
6. Plot effective diameter vs. time
7. Compare with fume measurements
8. Investigate filter by SEM.

CHEMISTRY OF FUME FORMATION

Evolution of sodium vapor:

$$Na_2CO_3 + 2\,C \rightarrow 2\,Na + 3\,CO$$

$$Na_2CO_3 + \tfrac{1}{4}\,Na_2S \rightarrow \tfrac{1}{4}\,Na_2SO_4 + CO_2 + 2\,Na$$

Condensation of sodium carbonate fume:

$$2\,Na + \tfrac{1}{2}\,O_2 \rightarrow Na_2O$$

$$2\,Na + CO_2 \rightarrow Na_2O + CO$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$

Reaction with sulfur gases:

$$Na_2CO_3 + SO_2 + \tfrac{1}{2}\,O_2 \rightarrow Na_2SO_4 + CO_2$$

$$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2$$

Other fume reactions:

$$NaCl\ (l) \rightarrow NaCl\ (g)$$

$$Na_2CO_3 + H_2O \rightarrow CO_2 + NaOH$$

Performance Improvement of the Kraft Recovery System Through Smelt Solidification

Student: *Bernard Chascin*

Advisor: *Jeff Empie*

Objective:

Determine the technical feasibility of solidifying smelt by a continuous process prior to dissolving in water to make green liquor.

Incentives:

- *Elimination of potential for smelt-water explosions*
- *Recovery of energy lost from the dissolving tank vent stack*
- *Decrease of TRS emissions*
- *Elimination of the need for shatter jet steam*
- *Deadload reduction through improved control of green liquor concentration*

TECHNICAL ISSUES

- *Equipment configuration*
- *Optimum temperature*
- *Materials of construction*
- *Energy recovery potential*
- *Dregs removal strategy*

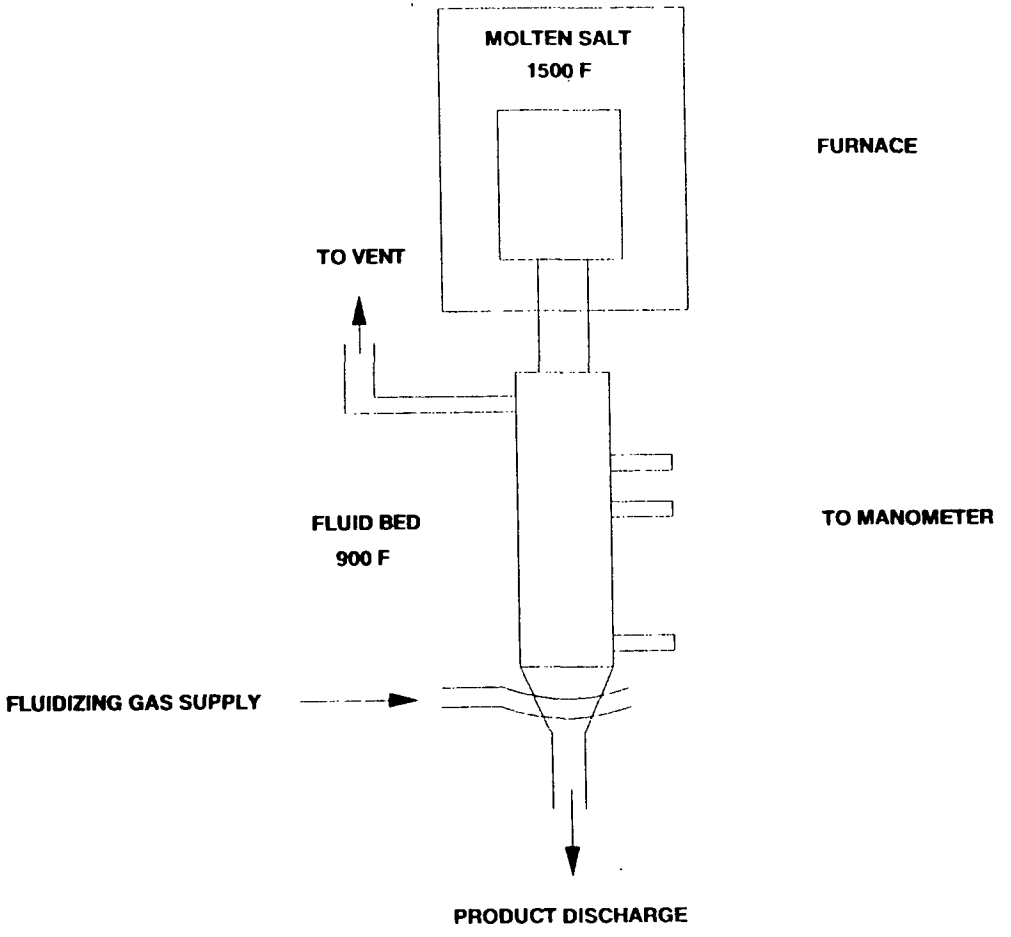
Accomplishments

- *Calculations favor fluidized bed crystallization concept*
- *Laboratory scale equipment designed and fabricated*
- *Construction in progress*

LABORATORY APPARATUS

FOR

SMELT SOLIDIFICATION



IPST Project 3671 - NCASI Funded

Feasibility of Thermal Destruction of Chlorine-Containing Concentrates from Closed Cycle Processes

Overview of 1st Year Results

Ken Nichols
IPST

Objective: Evaluate feasibility for thermal destruction of chlorine containing concentrated streams in a device other than the recovery furnace.

I. Characterization of concentrates
   - chemical
   - physical

II. Combustion behavior of concentrates
   - burning rates
   - fate of chlorine
   - ash characteristics

III. Review of incineration technology

IV. Definition of Practical Process Concepts

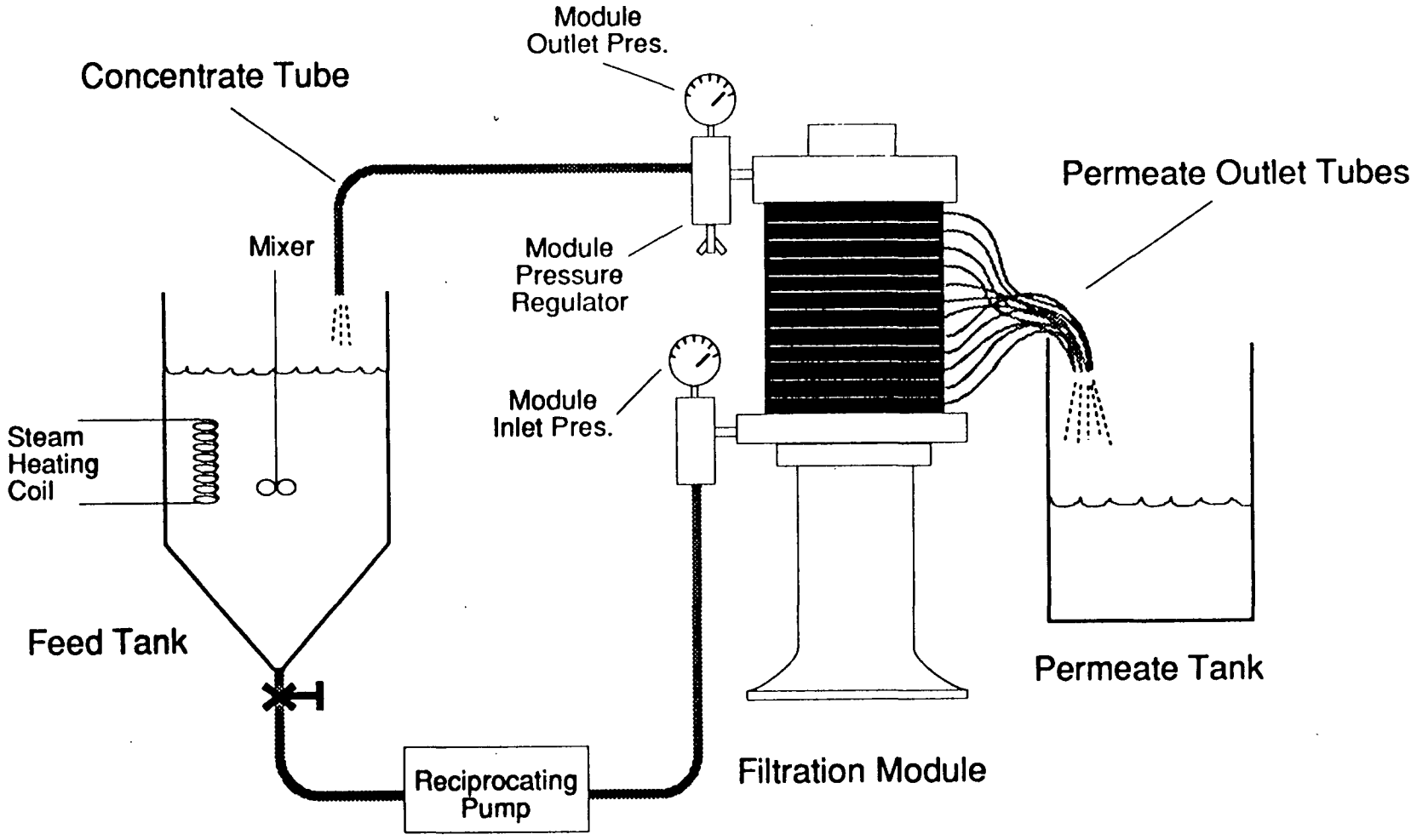


Figure 1. Schematic of Laboratory-Scale Filtration Equipment.

TABLE 1. Filtration Results: Mill A C/D Effluent			
	Untreated	UF(X38)[a]	RO(X40)
Total Solids mg/L	2,690	12,300(12.0%)[b]	68,800(63.9%)
Color, C.U.	1,060	19,500(48.4%)	36,000(84.9%)
Total Organic Carbon, mg/L	461	3,900(22.3%)	9,320(50.5%)
Chlorine, mg/L	985	2,480(6.63%)	26,500(67.3%)
Organic Chlorine, mg/L	100	980(25.8%)	2,740(68.5%)
Sodium, mg/L	366	675(4.85%)	9,780(66.8%)
Sulfur, mg/L	32	226(18.6%)	764(59.7%)

[a] concentration factor,
feed volume/concentrate volume

[b] percentage removal

TABLE 2. Filtration Results: Mill A E1 Effluent			
	Untreated	UF(X31)[a]	RO(X27)
Total Solids, mg/L	4,090	62,900(49.6%)[b]	92,800(84.0%)
Color, C.U.	14,800	386,000(84.1%)	334,000(83.6%)
Total Organic Carbon, mg/L	1,165	29,500(81.7%)	24,900(79.2%)
Chlorine, mg/L	953	5,770(19.5%)	14,300(55.6%)
Organic Chlorine, mg/L	104	1,300(40.3%)	2,130(10.7%)
Sodium, mg/L	736	5,490(24.1%)	19,200(96.6%)
Sulfur, mg/L	18.4	371(65.0%)	464(93.4%)

[a] concentration factor,
feed volume/concentrate volume

[b] percentage removal

Table 5. Elemental Composition of Concentrates, Moisture Free Basis

	Mill A C/D		*Mill A E1*		*Mill B C/D*		*Mill B E1*		*Other Fuels*		
	UF	RO	UF	RO	UF	RO	UF	RO	BLS[a]	MSW[b]	Coal[c]
C (total)	33.5	15.7	47.9	30.5	32.2	18.12	42.4	24.4	39.0	34.2	77.7
C (carbonate)	0.03	0.02	0.18	0.47	0	0.03	0.24	0.73			
H	2.54	2.24	3.58	2.59	2.38	2.53	3.37	2.53	3.8	4.5	5.0
O	31.2	22.2	30.1	26.8	31.7	22.9	34.8	26.3	33.0	27.1	6.2
Cl (total)	20.1	38.6	9.17	22.7	19.4	45.3	7.76	20.8	0.6	0.7	
Cl (organic)	7.95	3.98	6.80	2.30	4.76	6.78	5.76	2.19			
Na	5.49	14.2	8.73	20.7	4.49	11.01	11.39	26.8	18.6		
K	0.26	0.73	0.04	0.13	0.50	1.47	0.06	0.15	1.2		
S	1.84	1.11	0.59	0.50	2.91	2.27	0.58	0.57	3.6	0.3	1.6
Other Inorganic									0.2	32.6	8.0
Na/Cl Molar Ratio	0.42	0.57	1.47	1.41	0.36	0.37	2.26	1.99	4.80		
Heating Value KJ/Kg[d]	12,400	4,300	19,200	11,600	12,000	5,560	15,300	8,480	15,400	10,400	32,300
Organic/ Inorganic Ratio	4.30	0.83	5.25	1.50	3.77	1.03	4.40	1.21	3.24	2.02	10.9

[a] Black Liquor Solids (Adams and Frederick, 1988)
[b] Municipal Solid Waste (Seeker, et al., 1987)
[c] Bituminous Coal (Reid, et al. 1973)
[d] Determined by Bomb Calorimeter

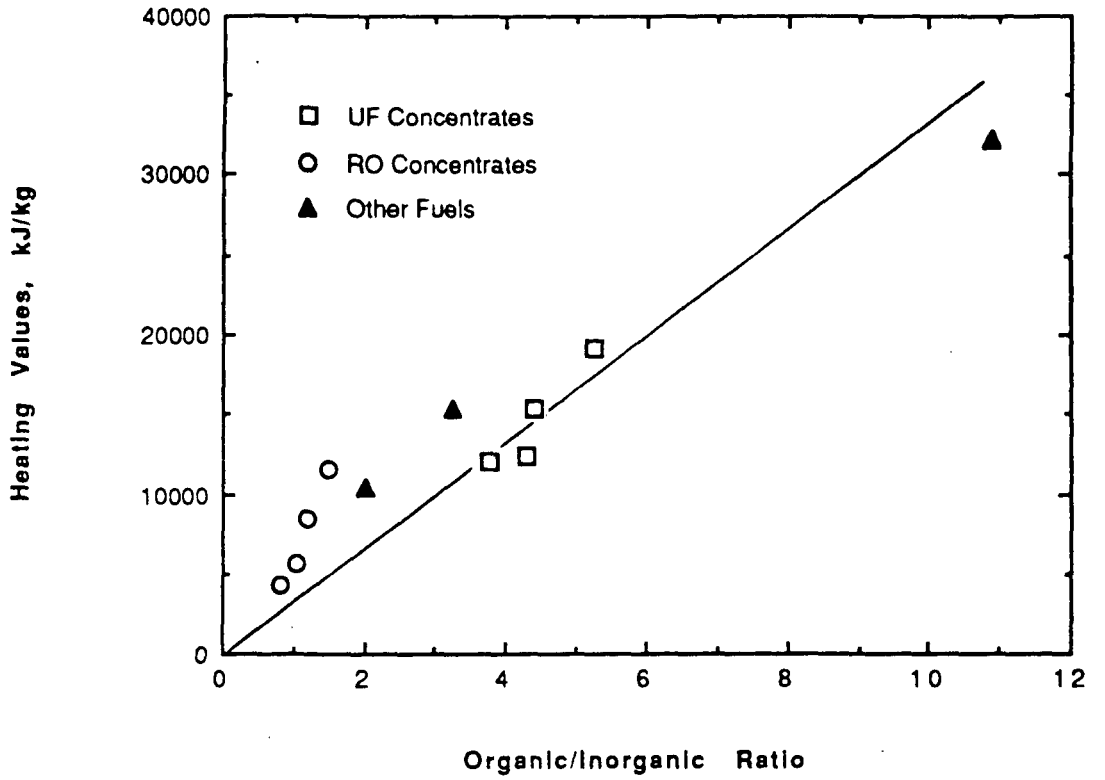


Figure 2. Higher Heating Value Values of the Concentrates.

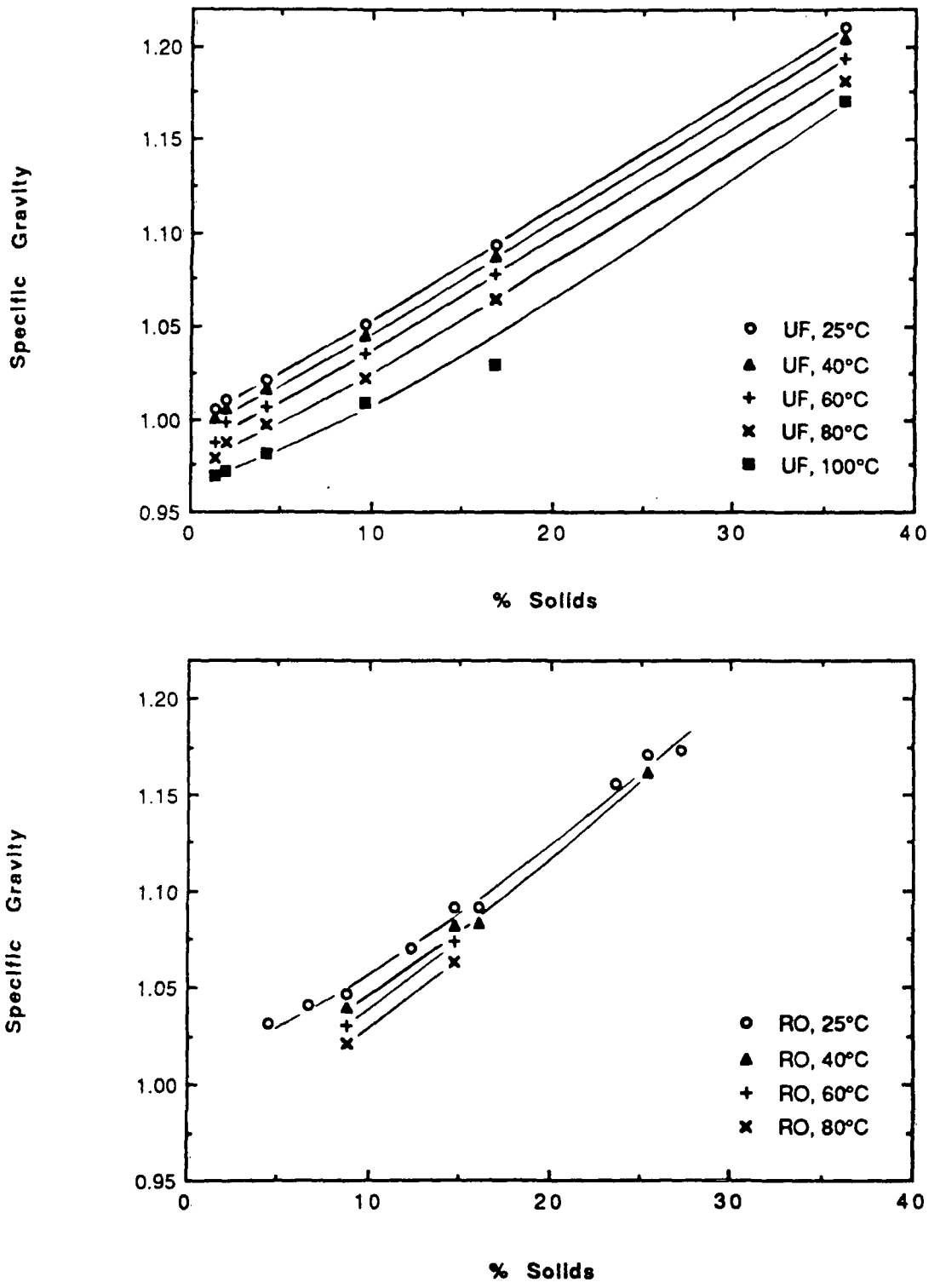
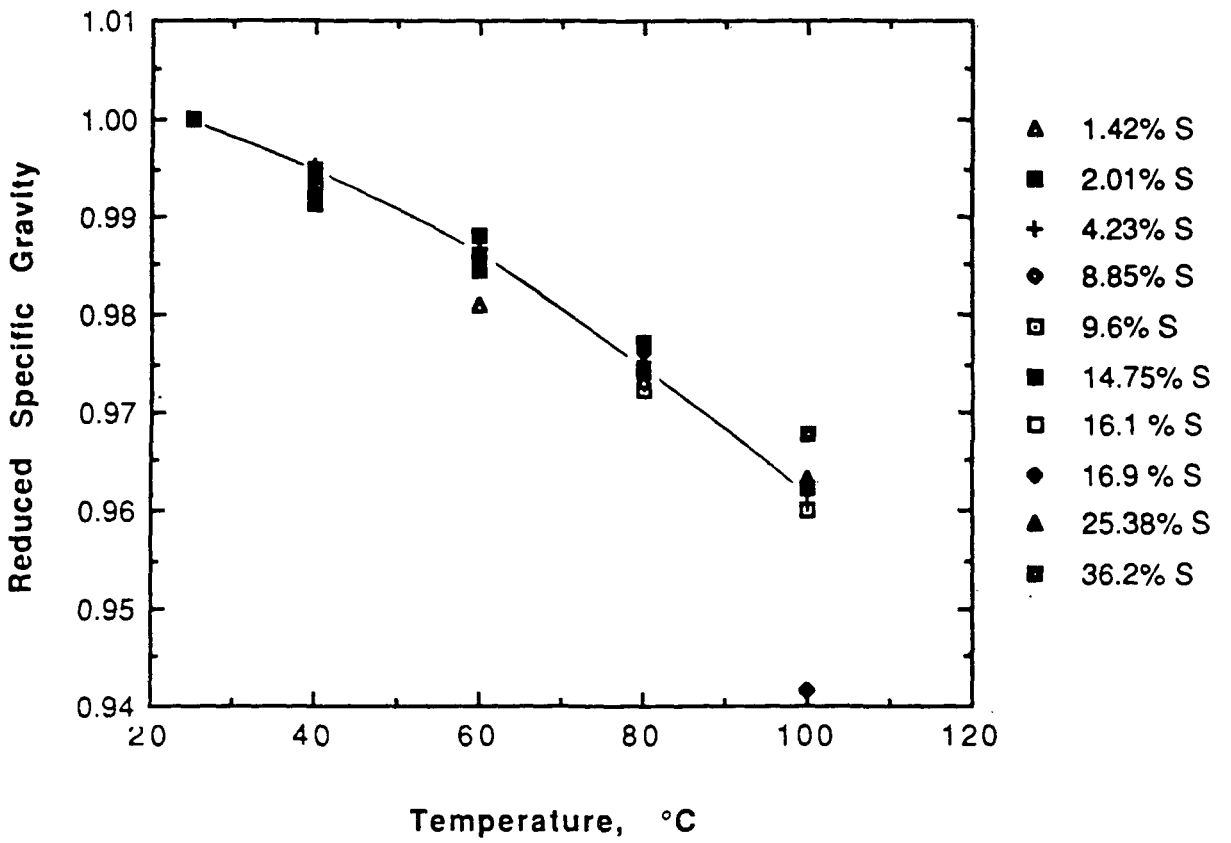
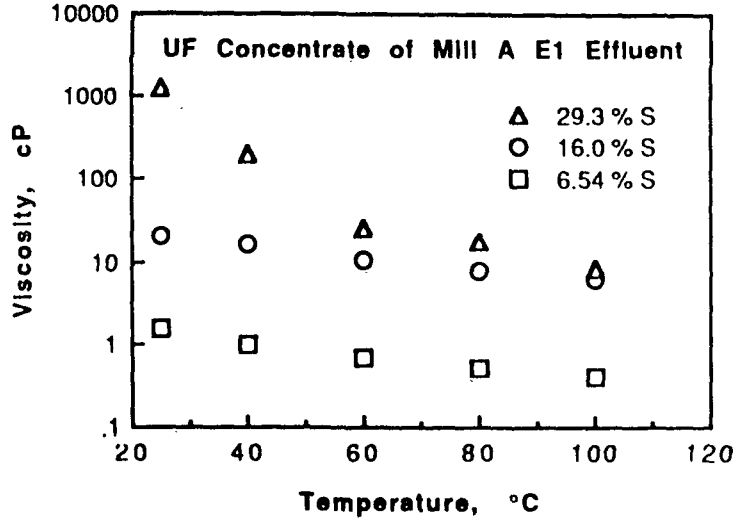
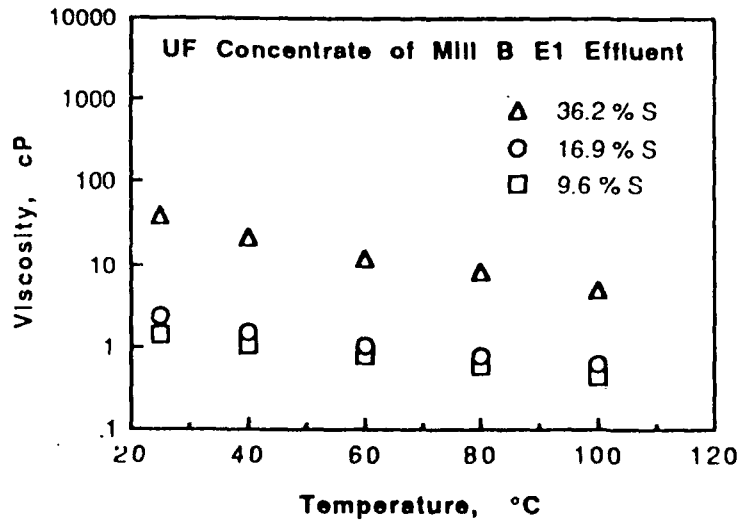


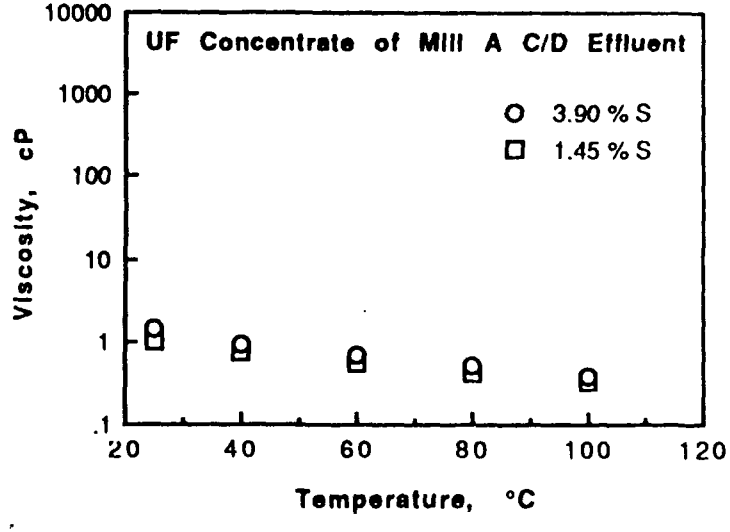
Figure 3. Specific Gravity Values of the Concentrates.

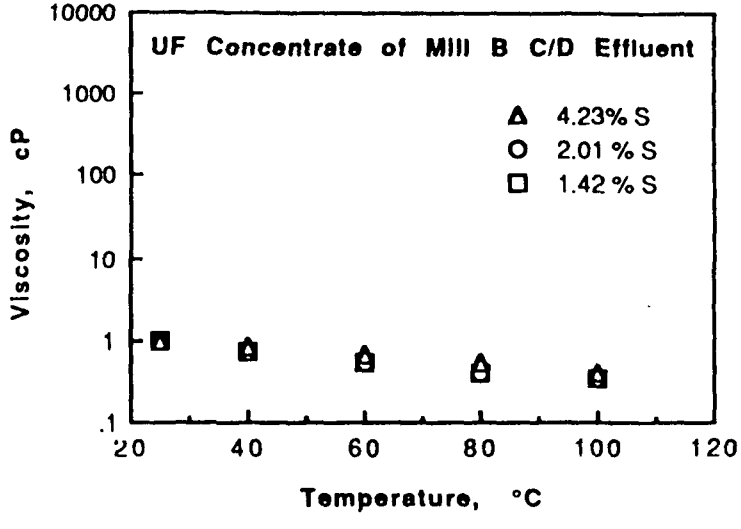


Reduced Specific Gravity of the Concentrates.

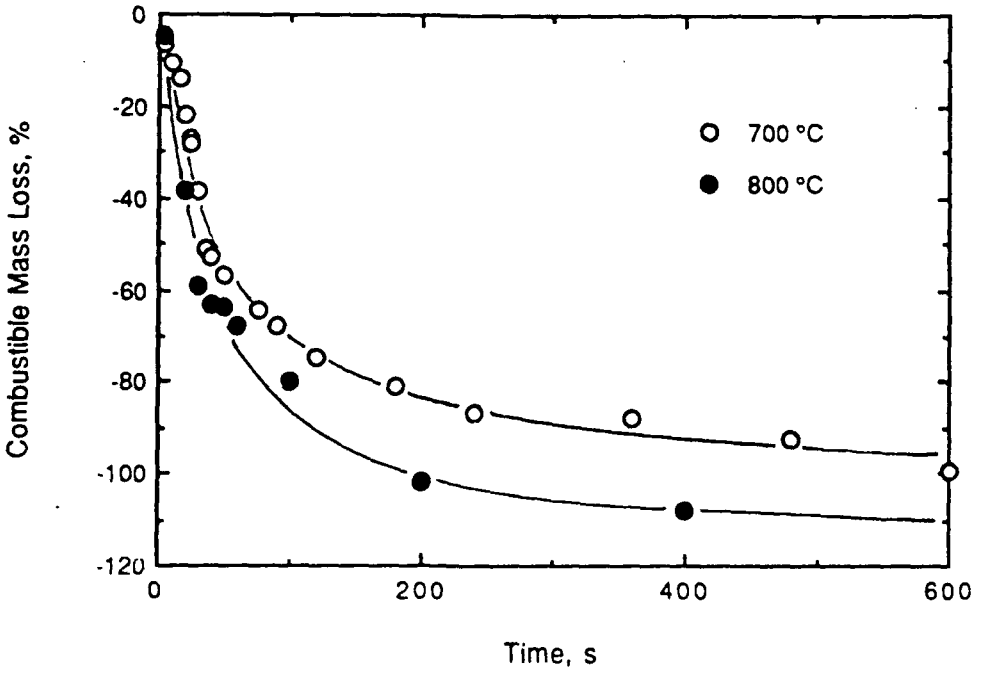




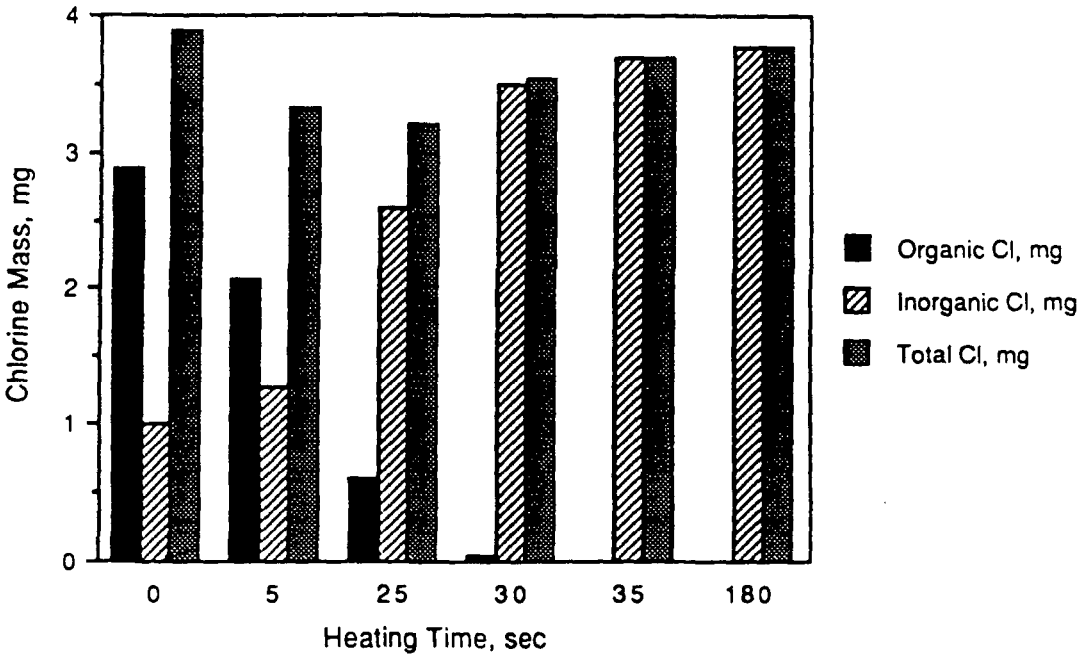




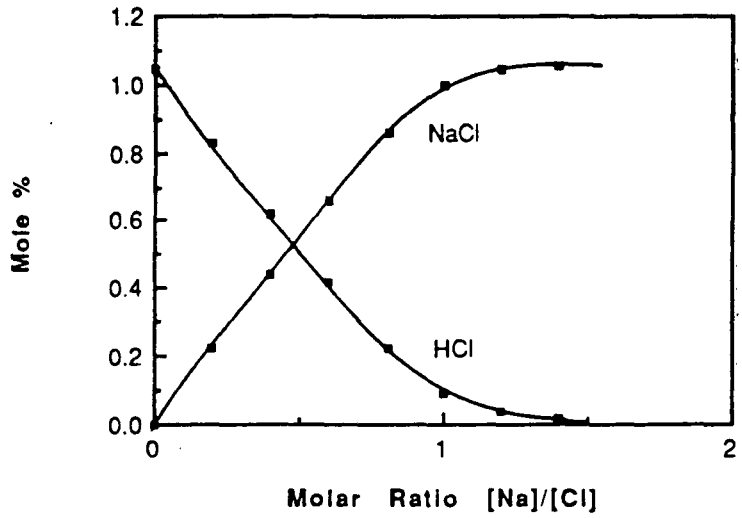
Viscosity Values of the UF Concentrates.



Isothermal mass loss curve, UF concentrate of E1 effluent (Mill B), 700 °C and 800 °C in air.



Trapping of chlorine during heating of UF concentrate of E1 effluent (Mill B), 700 °C in air.



Prediction of fate of chlorine based on chemical equilibrium.

Ash Characteristics

- ash represents approx 20 wt% of UF concentrate, and approx 55 wt% of RO concentrate

- consists primarily of NaCl with some NaSO4

	UF concentrates	RO concentrates
1st melting	700-800 °C	600-650 °C
complete melting	840-1050 °C	750 °C

Summarizing:

- feasibility is high for thermal destruction of UF concentrates of E1 effluent

- concentrate solids similar to BLS in:
  - chemical composition (except Cl)
  - heating value
  - viscosity (not very predictable)
  - density (very predictable)

- concentrates consist of approx:
  - 40 wt% volatiles
  - 40 wt% char
  - 20 wt% inorganic (NaCl)

- overall burning modeled well by two part model (1st order in both devol. and char burning)

- Na/Cl ratios are 1.5-2.3, results in chlorine trapping, implies significantly decreased opportunity for PCDD/PCDF emissions

- thermal degradation of organic Cl occurs 2-5 X faster than degradation of total organics

- ash melting points are near 800 °C and higher

Recommendations to NCASI for Phase II Funding

Fluidized Bed Combustion

- *Destroys organics while maintaining inorganics in a solid state*
- *Need to demonstrate feasibility on a small scale*
- *Provides adequate temperature control and residence time*
- *Determine emissions levels of HCl and PCDD/PCDF*

Recovery Furnace Combustion

- *Mix UF concentrate with weak black liquor prior to test burn*
- *Physical/Chemical properties and HHV are similar to black liquor*
- *No furnace derating*
- *Determine emissions levels and Cl mass balance*

Development of Kraft Recovery Furnace Modeling Capability

Jeff Empie

A Program to

Develop a Useful Modeling Capability of the Kraft Recovery Boiler

with

Continuation of Supporting Studies on Black Liquor Combustion Fundamentals

GOAL

Modeling Capability for Kraft Recovery Furnace

Useful for Increasing Energy Efficiency and Productivity of Kraft Recovery Boilers

through

Design and Operational Changes

Current Status

Improved Mechanistic Models Available

Additional Mechanistic Requirements Defined

Current Computational Fluid Dynamics (CFD) Codes Inadequate

Industry Becoming Impatient

Needs

- *Completion of Mechanistic Models*
  - *Droplet Combustion*
  - *Char Bed Burning*
  - *Fume Formation/Sulfur Capture*
  - *Fume Deposition*

- *Rapid Availability of Useable Results - Fixed Flow Fields*

- *Advanced CFD Code for 3-D Model of Recovery Furnace*
  - *Gas Phase Jet Interaction*
  - *Multigridding Methodology*
  - *Rapid Convergence*

- *Global Simulation of Kraft Recovery Furnace*

- *Validation of Global Model*
  - *Physical Measurement*
  - *Operating Recovery Boiler*

International Team

IPST	*Jeff Empie* *Bob Horton* *Steve Lien* *Ken Nichols*
UBC	*Martha Salcudean* *Ian Gartshore*
Abo Akademie	*Jim Frederick*
T.M. Grace Co.	*Tom Grace*

Approved Program

Four-year, $3,015 Program Leading to the Development of a Validated, Global Modeling Capability of the Kraft Recovery Boiler.

Funded by: ***DOE-OIP***
IPST
API-RBC

	TOTAL $	*YEAR-ONE $*
DOE	*1,685,000*	*550,000*
IPST	*1,070,000*	*300,000*
API	*260,000*	*65,000*
	3,015,000	*915,000*

Milestones

Year 1

- *Single particle combustion model (Abo Akademie)*
- *Furnace combustion model with fixed velocity, temperature, and concentration fields*
- *CFD code for 2-D jet interaction with crossflow (UBC)*

Year 2

- *Quantification of char gasification rates and selectivity*
- *Understanding of fume formation processes*
- *Fume formation/Sulfur release model (Abo Akademie)*
- *Furnace diagnostics prototype for validating model*
- *CFD multigrid code for 2-D jet interaction with crossflow (UBC)*

Year 3

- *Sulfur capture model (Abo Akademie)*
- *Understanding of fume deposition phenomena*
- *Understanding of dynamics of char bed shape*
- *Furnace combustion model with fixed velocity and temperature fields*
- *Measurement (pointwise) of furnace cavity temperatures and velocities*
- *CFD multigrid code for 3-D jet interaction with crossflow (UBC)*

Year 4

- *Furnace combustion model with variable velocity, temperature, and concentration fields*
- *Non-isothermal CFD code (UBC)*

Budget - Year 1

	$1000			
	IPST	***DOE***	***API***	***TOTAL***
Recovery Furnace Model	*150*	*92*	*45*	*287*
CFD Code Development		*185*	*20*	*205*
Single Particle Combustion Model		*110*		*110*
Char Combustion	*90*	*88*		*178*
Model Validation	*60*	*75*	_	*135*
TOTAL	*300*	*550*	*65*	*915*

Year 2

	$1000			
	IPST	*DOE*	*API*	*TOTAL*
Recovery Furnace Model	*135*	*10*	*45*	*190*
CFD Code Development		*150*	*20*	*170*
Fume Formation/Sulfur Release Model		*115*		
Char Combustion	*80*	*100*		*180*
Fume Deposition	*60*	*70*		*130*
Model Validation	*80*	*90*	_	*170*
TOTAL	*355*	*535*	*65*	*955*

Year 3

Recovery Furnace Model	*135*	*10*	*45*	*190*
CFD Code Development		*150*	*20*	*170*
Sulfur Capture Model		*120*		*120*
Fume Deposition	*50*	*50*		*100*
Model Validation	*60*	*50*	_	*110*
	245	*380*	*65*	*690*

Year 4

Recovery Furnace Model	*135*	*20*	*45*	*200*
CFD Code Development		*150*	*20*	*170*
Model Validation	*35*	*30*		*65*
Technology Transfer	___	*20*	_	*20*
	170	*220*	*65*	*455*
PROGRAM TOTAL	*1,070*	*1,685*	*260*	*3,015*

Project Advisory Committee Meeting
Recovery Group
Dec. 14, 1990

Kraft Recovery Furnace Modeling
(Project 3605)
Robert R. Horton

Outline

Project Objective
Modeling Approach
Schedule
Discussion
Summary

Project Objective

Develop a Kraft recovery furnace modeling capability that can be used to improve furnace operation and design.

Approach

Develop a global model in phases beginning with simple but operational models.

Conduct parameter sensitivity studies using simplified models.

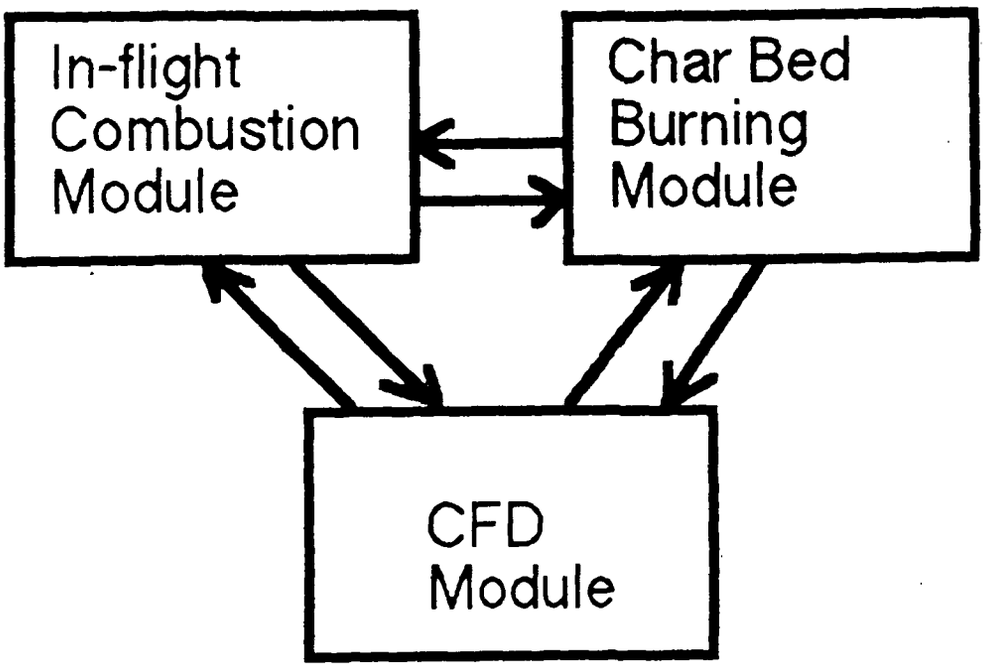
Minimize unnecessary calculations.

Determine trends of important variables.

Predict optimum operating ranges where possible.

Verify early predictions and trends with full scale simulation of global model and plant trial results.

Computer Program Flow Diagram



Gas Phase Fields

Calculations

The model uses mass, energy and momentum balances to predict concentrations, temperatures and velocities.(C_i, T, V_i Fields)

Interfacing the Modules

Information on mass, energy, and momentum sources and sinks must be transferred between modules of the model.

Physical properties and combustion rates can be determined from this information.

Model Development Schedule

Year 1

Model IF-1
In-flight Black Liquor Combustion
- fixed gas phase fields V_i, T, and C_i
- no mass, energy or momentum balances between gas and in-flight droplets

Model IF-2
In-flight Black Liquor Combustion
- satisfied component mass balances for C_i calculation in gas phase
- fixed gas phase V_i and T fields

Model CB-1
Char Bed Burning
- fixed fields V_i, T, and C_i
- fixed bed shape

Model CB-2
Char bed Burning
- fixed fields V_i, T, and bed shape
- satisfied component mass balances for C_i in gas region near bed

Year 2

Model C-1
Combustion model (integrated in-flight and bed models)

fixed gas phase V_i and T fields

satisfied component mass balances for C_i

Model IF-3
In-flight model with fixed V_i field

satisfied energy balance for T
satisfied mass balance for C_i

Model CB-3
Char bed model with fixed V_i field and bed shape

satisfied energy balance for T
satisfied mass balance for C_i

Year 3

Model C-2
Combustion model (integrated in-flight and bed models)
- fixed gas phase V_i and bed shape
- satisfied energy balance for T
- satisfied component mass balances for C_i

Model CB-4
Char Bed Model
- fixed V_i fields
- satisfied balances for C_i and T
- include bed movement and bed shape calculations

Model E-1
Emissions model
Incorporate sulfur and fume chemistry into model

Year 4

Model C-3
Combustion / CFD integrated Model
satisfied momentum, energy and mass balances

In-Flight Black Liquor Combustion Modeling

Major Features

Black Liquor Droplet Description

- Diameter (function of combustion stage and time)
- Composition (water, organics, inorganics)

Stages of Combustion

- Evaporation (heat transfer limited)
- Pyrolysis (heat transfer limited)
- Char Burning (mass transfer limited)
- Smelt Reactions

Flight Path

- Drag Coefficients
- Directional Velocity Components

Six Month Work Plan

In-flight Models IF-1 and IF-2

Currently Developing IF-1
All fields fixed, i.e. combustion calculations do not affect gas phase properties

No iteration; gas velocities, temperatures and concentrations are fixed and combustion of black liquor droplets is modeled without feeding back the information.

Simulation Case Studies

- definition of important liquor parameters
- effects of spray size and velocity on carryover
- sensitivity to furnace temperatures and O_2 conc.
- sensitivity of carryover predictions to features of flow patterns

Limitations

- fixed flow fields
- important not to over-conclude

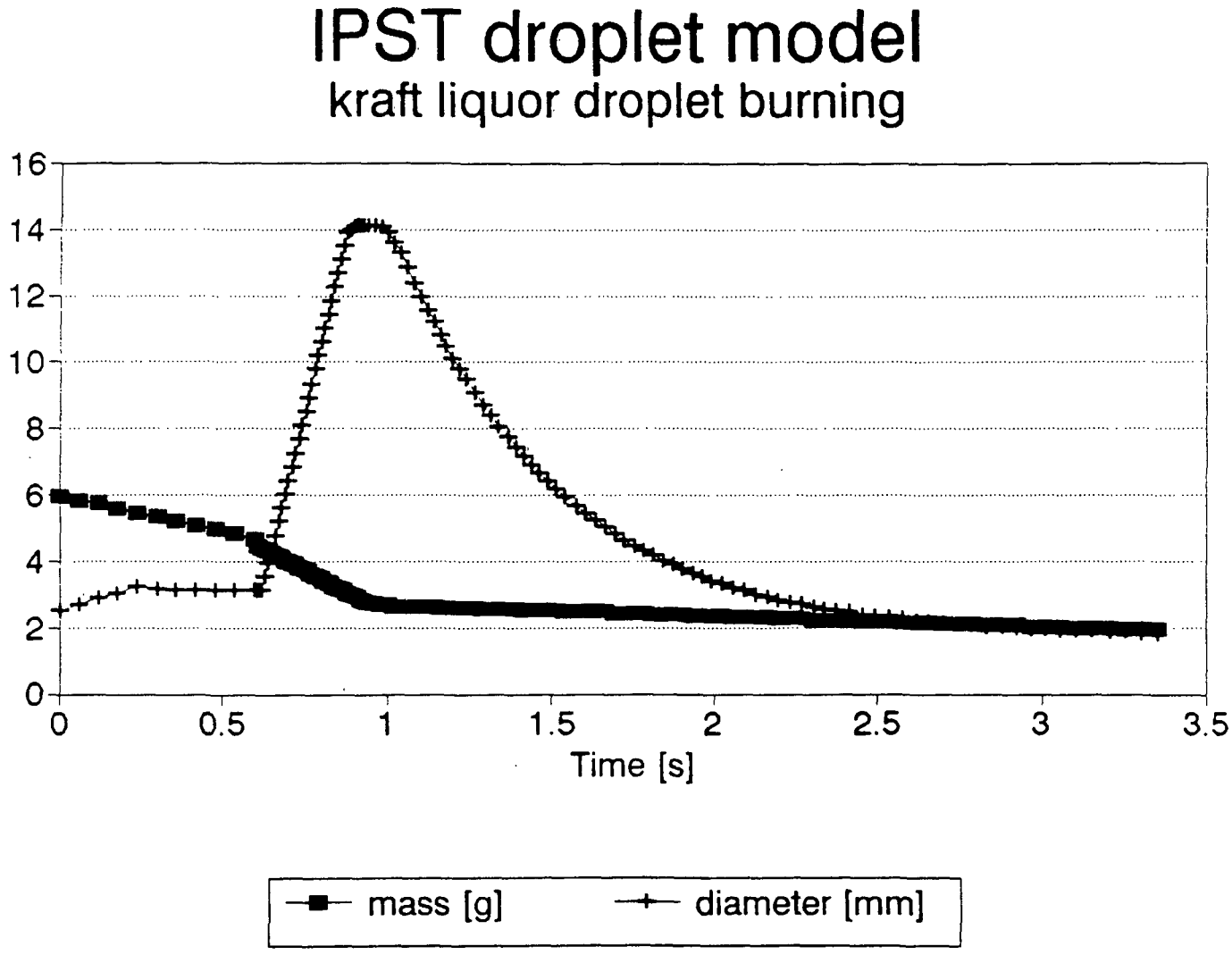
Model IF-2
Close Component mass balances
Gas Temperatures and velocities are fixed

Gas phase concentrations are computed via stoichiometry and mass balances

Will be able to predict zones of heat generation

Simulations

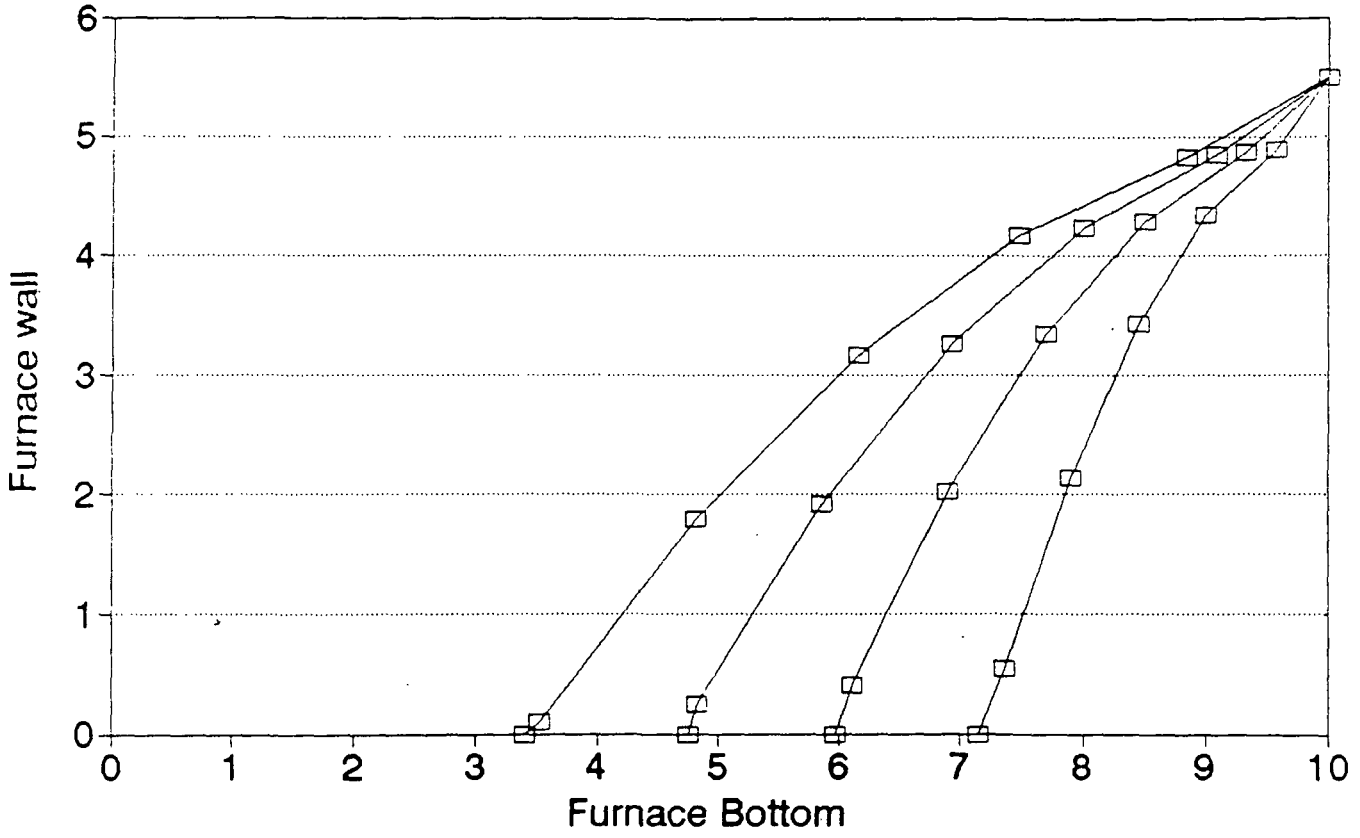
- Insight into O_2 depleting reactions
- Importance of CO_2 gasification in-flight
- Preliminary evaluation of O_2 enrichment



Droplet diameter vs. time for furnace temperature of 1100°C

IPST droplet model

kraft liquor droplet burning



Droplet trajectories for a 2.5mm droplet at 3, 4, 5, and 6 m/s nozzle velocities

Areas for Investigation

Convective Heat transfer calculations

Importance of droplet surface temperature

Description of radiative heat transfer and emmissivity

Importance of CO_2 char gasification in low O_2 areas

Smelt reactions

Summary

Recovery furnace modeling project will span four years.

IPST will concentrate on combustion modeling; CFD code will be developed by UBC.

Meaningful results will become available during the course of the project.

Sensitivity studies will allow us to optimize computational efficiency of the global model.

Validation of Recovery Furnace Modeling Capability

Jeff Empie

Objective: ***Develop a practical technique and necessary equipment for pointwise determination of flue gas temperature and velocity in the furnace cavity of an operating recovery boiler.***

Intrusive or Non-Intrusive?

Velocity measurement requirements:	***Local***
	Magnitude
	Direction
Non-intrusive methods:	***Average values over line-of-sight***
	Direction not determined
Intrusive methods:	***Probe subject to deposition***
	High probe corrosion rates
Either method:	***Unsteady flue gas velocities***
	Limited furnace access locations

Conclusion

Go Intrusive

- *Problems are operational*
- *Non-intrusive methods problems are fundamental*

Tasks / Schedule

		Target Date
1.	*Literature Survey*	*1/15/91*
2.	*Probe Concept and Design*	*3/31/91*
3.	*Probe Construction*	*5/31/91*
4.	*Laboratory Furnace Testing*	*7/31/91*
5.	*In-Flight Char Bed Reactor Testing*	*10/31/91*
6.	*Recovery Boiler Testing*	*9/30/92*

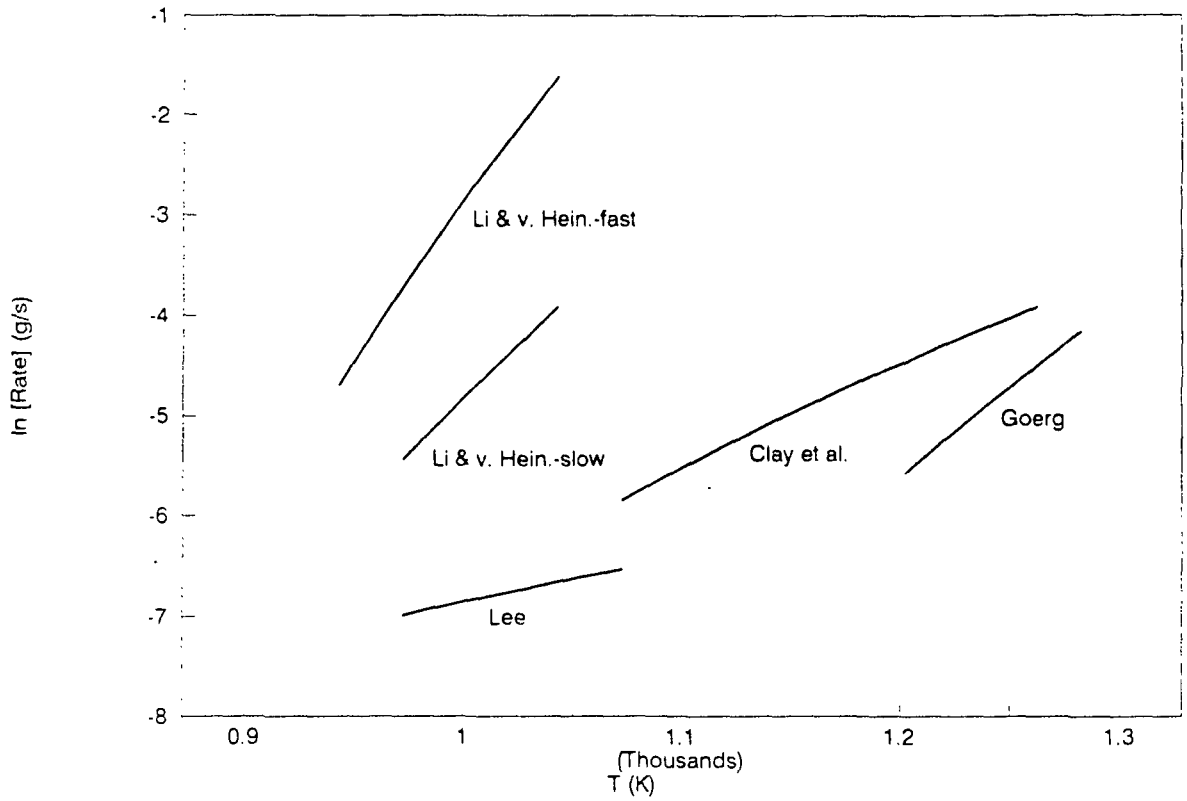
CO_2 Gasification of Kraft Char

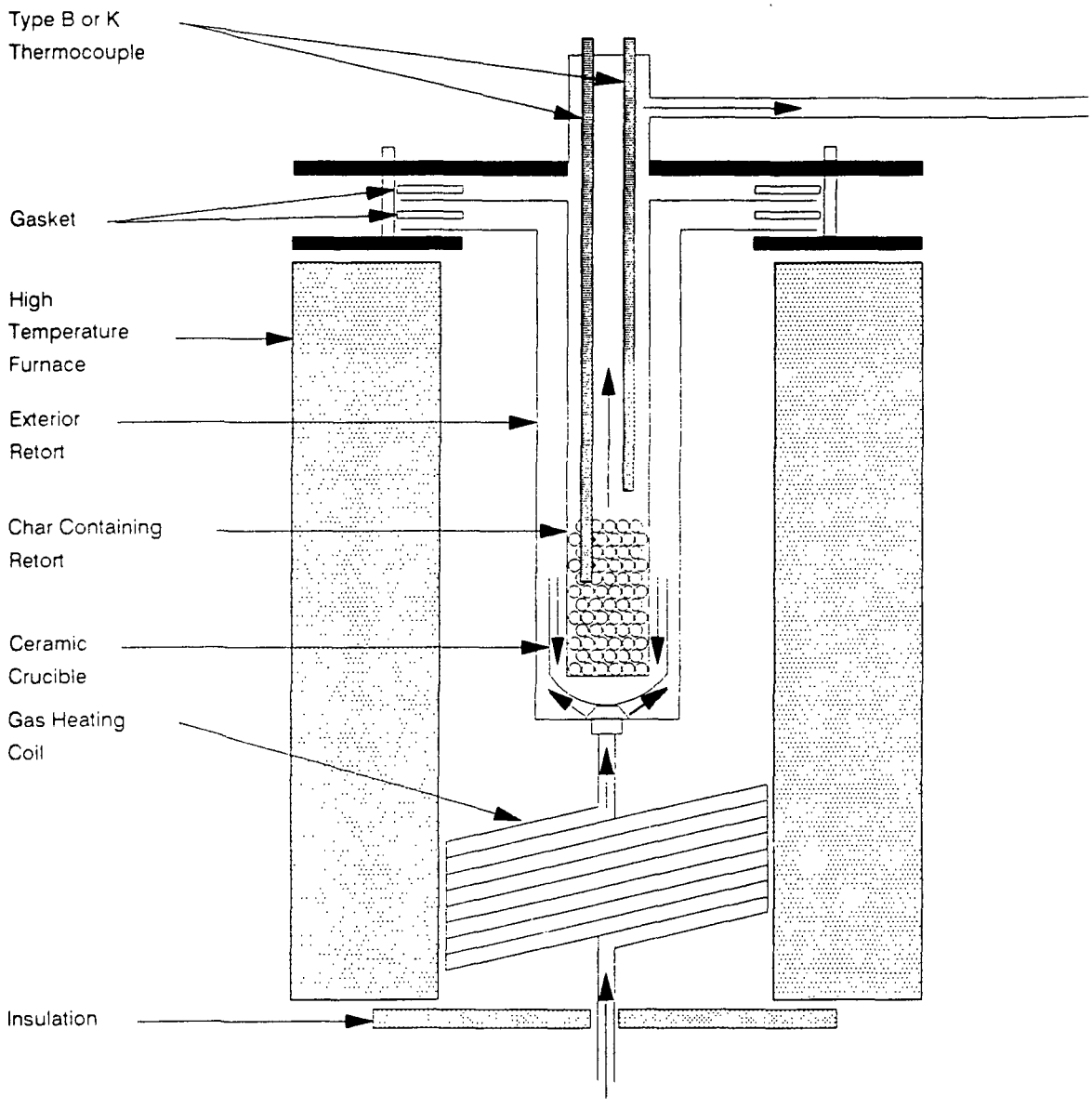
Student: *Stacy Lee*

Advisor: *Ken Nichols*

Objectives:

- *Determine Inherent Reaction Kinetics for CO_2 Gasification of Kraft Char (600°-1200°C)*
- *Establish Transition Temperature where Mass Transfer Becomes Rate Limiting*
- *Develop Rate Expression for Recovery Furnace Model*


-1
-2
-3
-4
-5
-6
-7
-8
ln [Rate] (g/s)
Li & v. Hein.-fast
Li & v. Hein.-slow
Clay et al.
Goerg
Lee
0.9
1
1.1
1.2
1.3
(Thousands)
T (K)


Type B or K
Thermocouple
Gasket
High
Temperature
Furnace
Exterior
Retort
Char Containing
Retort
Ceramic
Crucible
Gas Heating
Coil
Insulation

AN EXAMINATION OF THE MECHANISMS CONTROLLING THE DROPLET SIZE DISTRIBUTION OF A SPRAY

T.M. SPIELBAUER
C.K. AIDUN
T.N. ADAMS
J.D. LINDSAY

- Thesis Objectives
- Sheet Break Up Mechanisms
- Experimental System
- Results
  - Perforation Number Density
  - Source of Perforations
- Strand Break Up Theories
- Future Work

Initial droplet size is important:

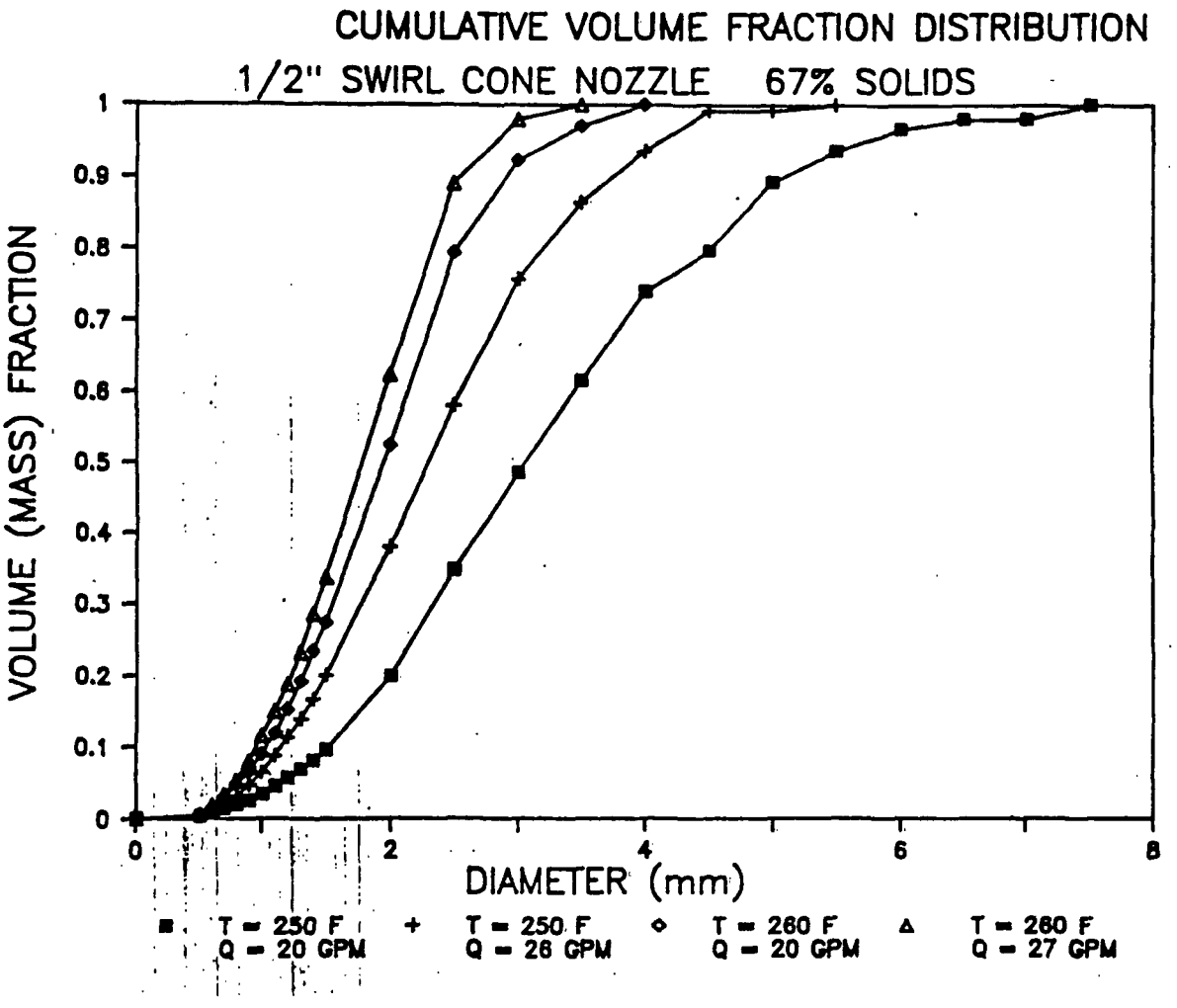
- combustion behavior
- carry over
- sulfur release rates
- NOx formation ?

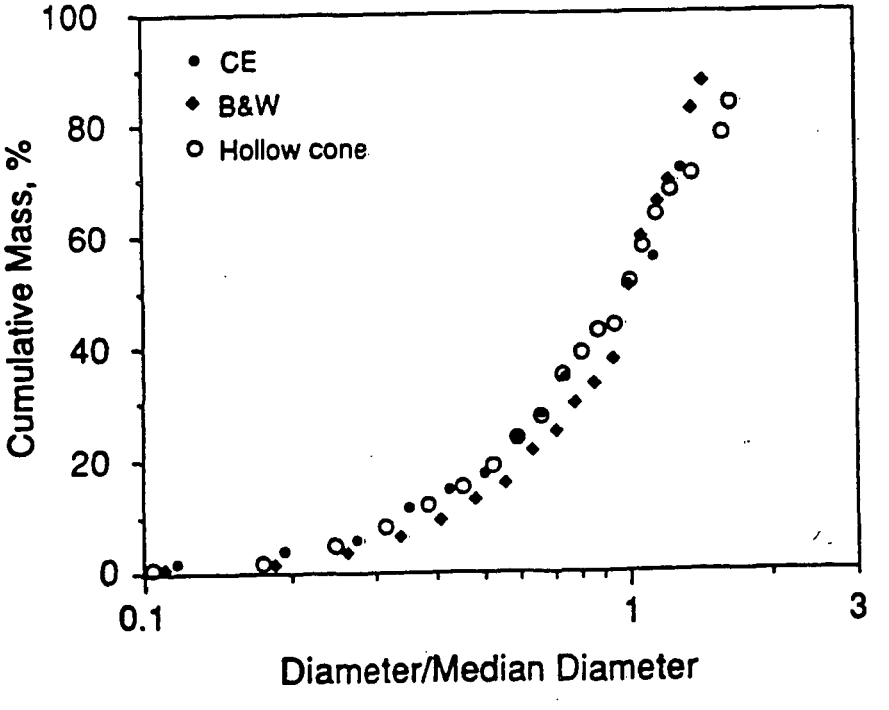
Black liquor firing conditions are easily controllable:

- nozzle style
- size and number of nozzles
- liquor firing temperature

THESIS OBJECTIVES

- Why Does a Distribution of Drop Sizes Exist?
  - Determine Mechanisms of Sheet Break Up
  - Examine Strand Break Up Processes
  - Study Effects of Operating Conditions
  - Develop Analytical Predictions


CUMULATIVE VOLUME FRACTION DISTRIBUTION
1/2" SWIRL CONE NOZZLE 67% SOLIDS
VOLUME (MASS) FRACTION
DIAMETER (mm)
T = 250 F Q = 20 GPM
T = 250 F Q = 26 GPM
T = 260 F Q = 20 GPM
T = 260 F Q = 27 GPM

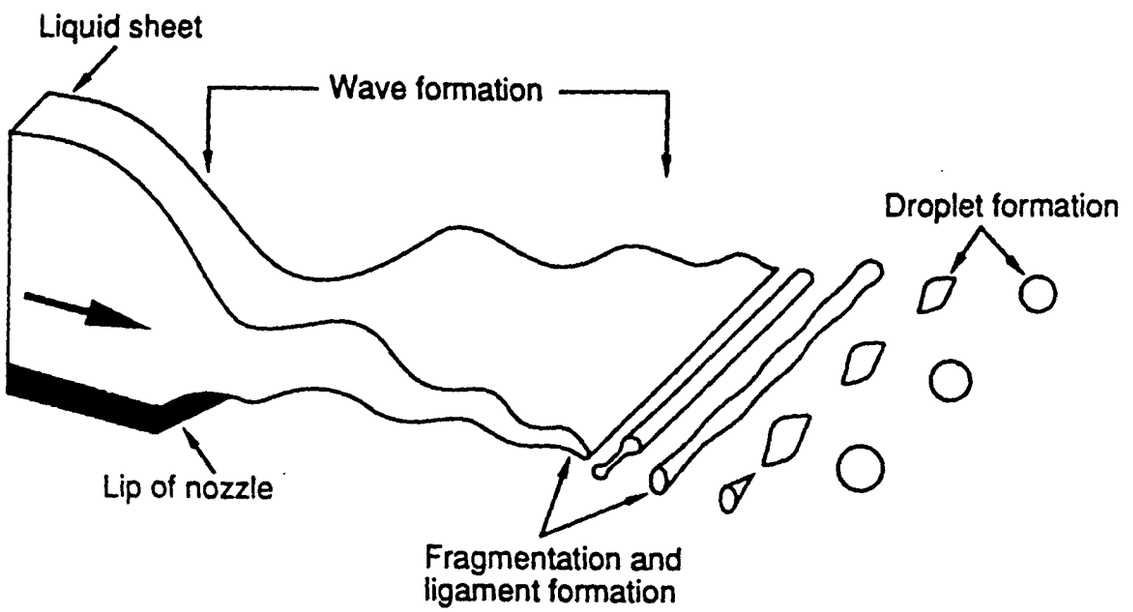

CE
B&W
Hollow cone
Cumulative Mass, %
Diameter/Median Diameter

The spraying process:

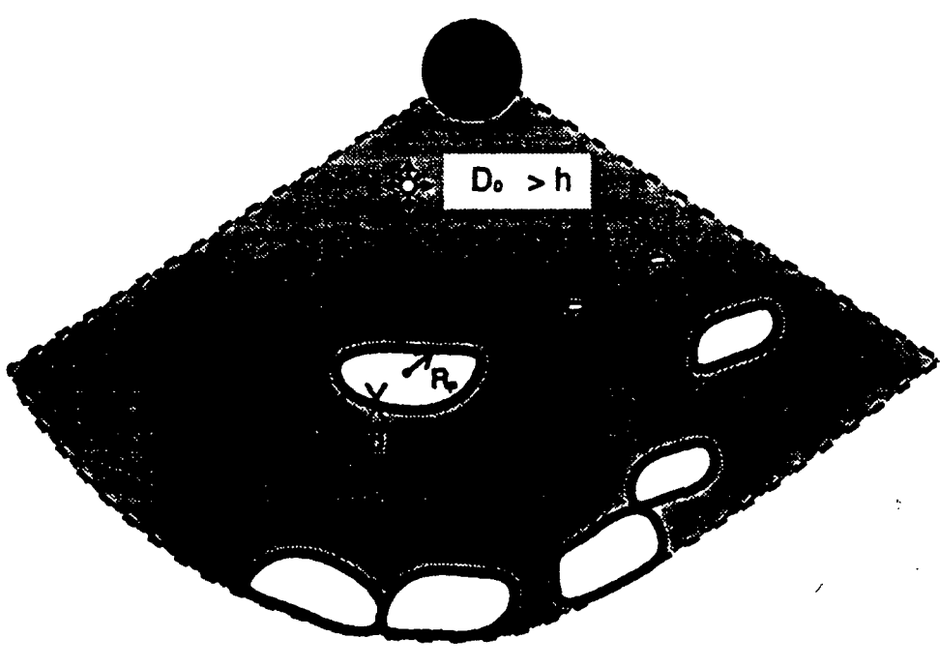
- a sheet of fluid is formed
- the sheet breaks up into strands
- the strands break up into droplets

Sheet break up:

- wave growth
- perforations



Perforation Mechanism

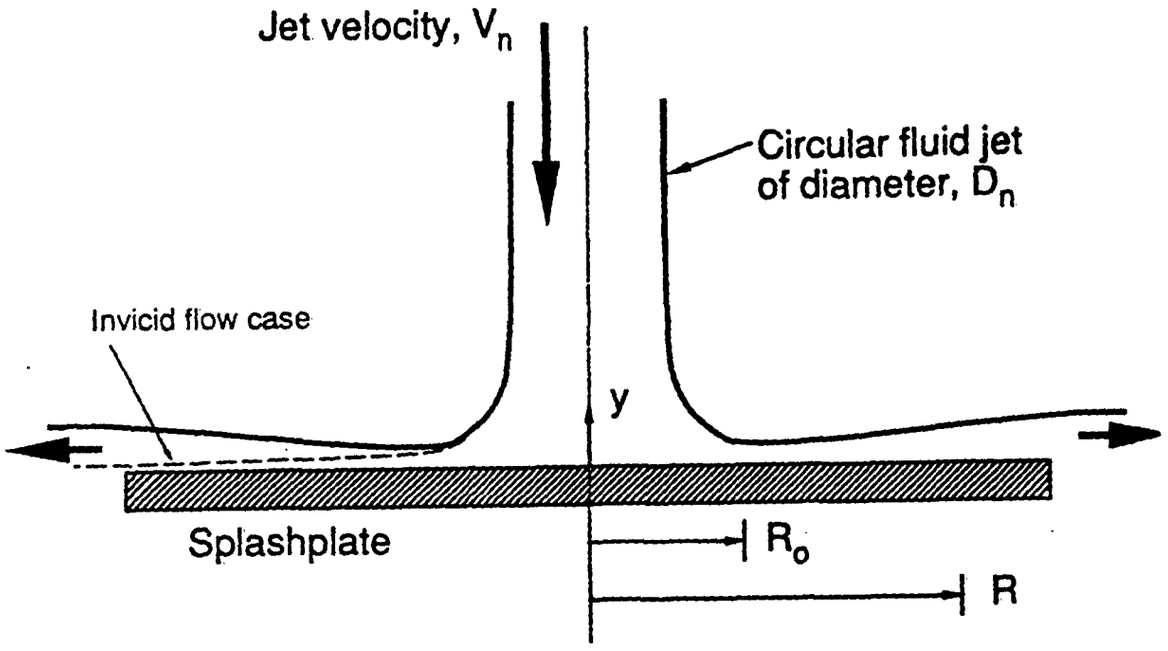


EXPERIMENTAL OPERATING CONDITIONS

- Model Fluids
  - Known physical properties
  - Easy to work with
- Simple Nozzle Geometry
- High Speed Video Imaging

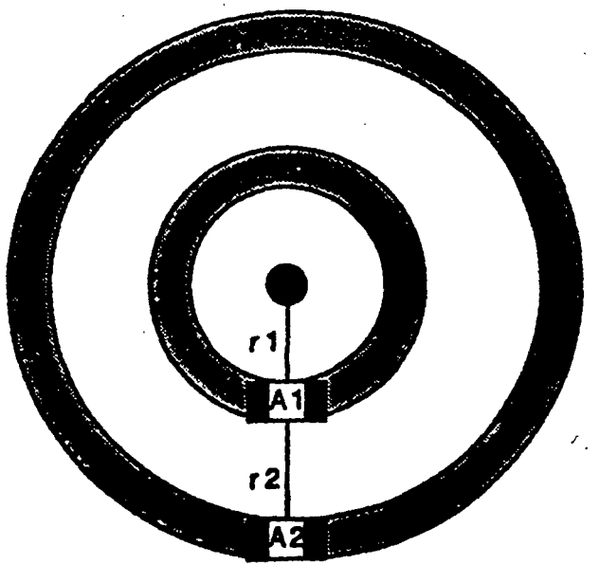
Xybion ISG-250 Camera

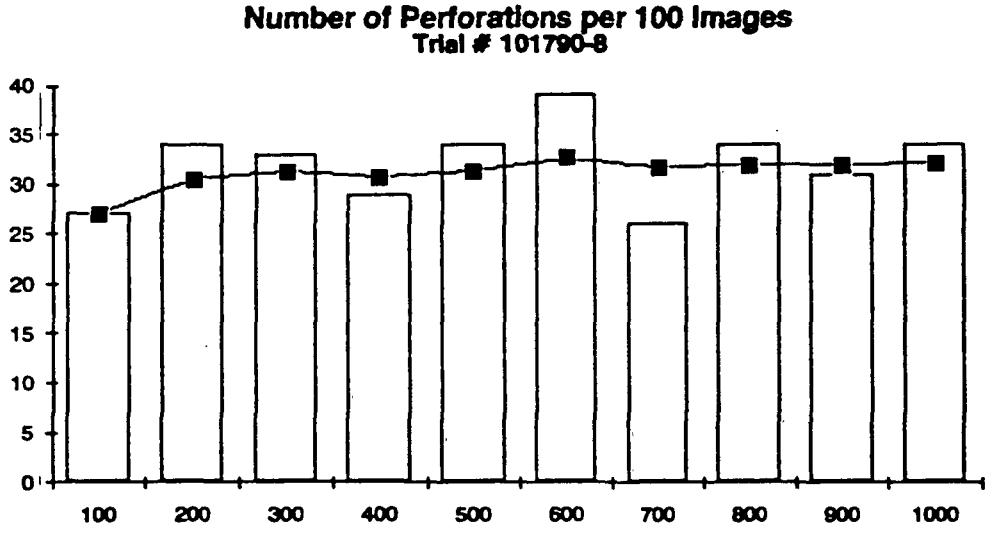
- 30 Images per Second
- Flexible Gating
  - Short exposure times (20 nsec - 20 msec)
  - Multiple exposures possible
- Easy to Operate

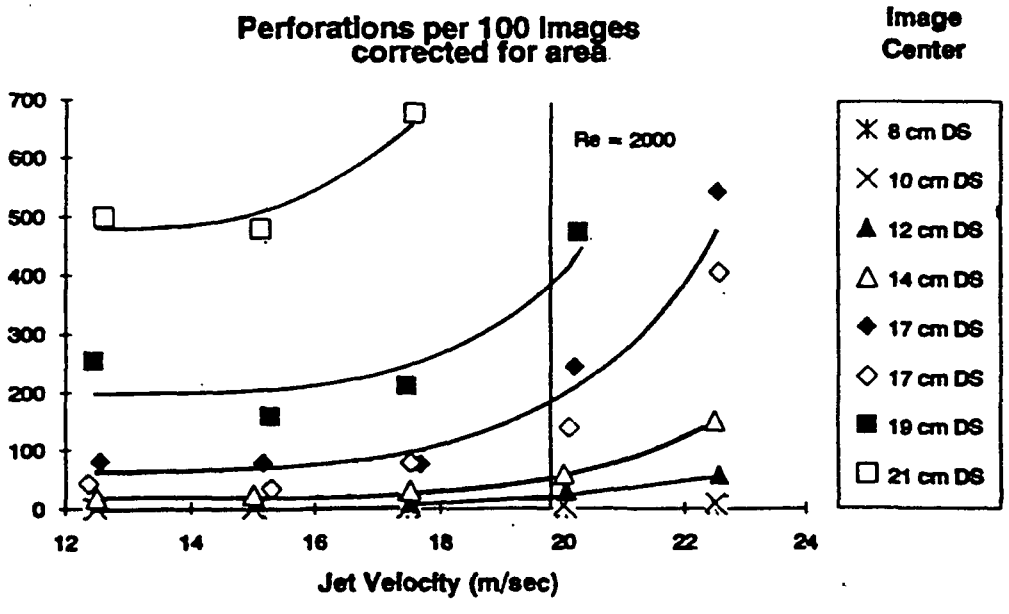


Number Density of Perforations

- high speed video imaging (5 μs exposures)
- 1000 images viewed at each condition
- perforation count normalized for area




Number of Perforations per 100 Images
Trial # 101790-8
40
35
30
25
20
15
10
5
0
100
200
300
400
500
600
700
800
900
1000


Perforations per 100 Images
corrected for area
Image
Center
Re = 2000
8 cm DS
10 cm DS
12 cm DS
14 cm DS
17 cm DS
17 cm DS
19 cm DS
21 cm DS
700
600
500
400
300
200
100
0
12
14
16
18
20
22
24
Jet Velocity (m/sec)

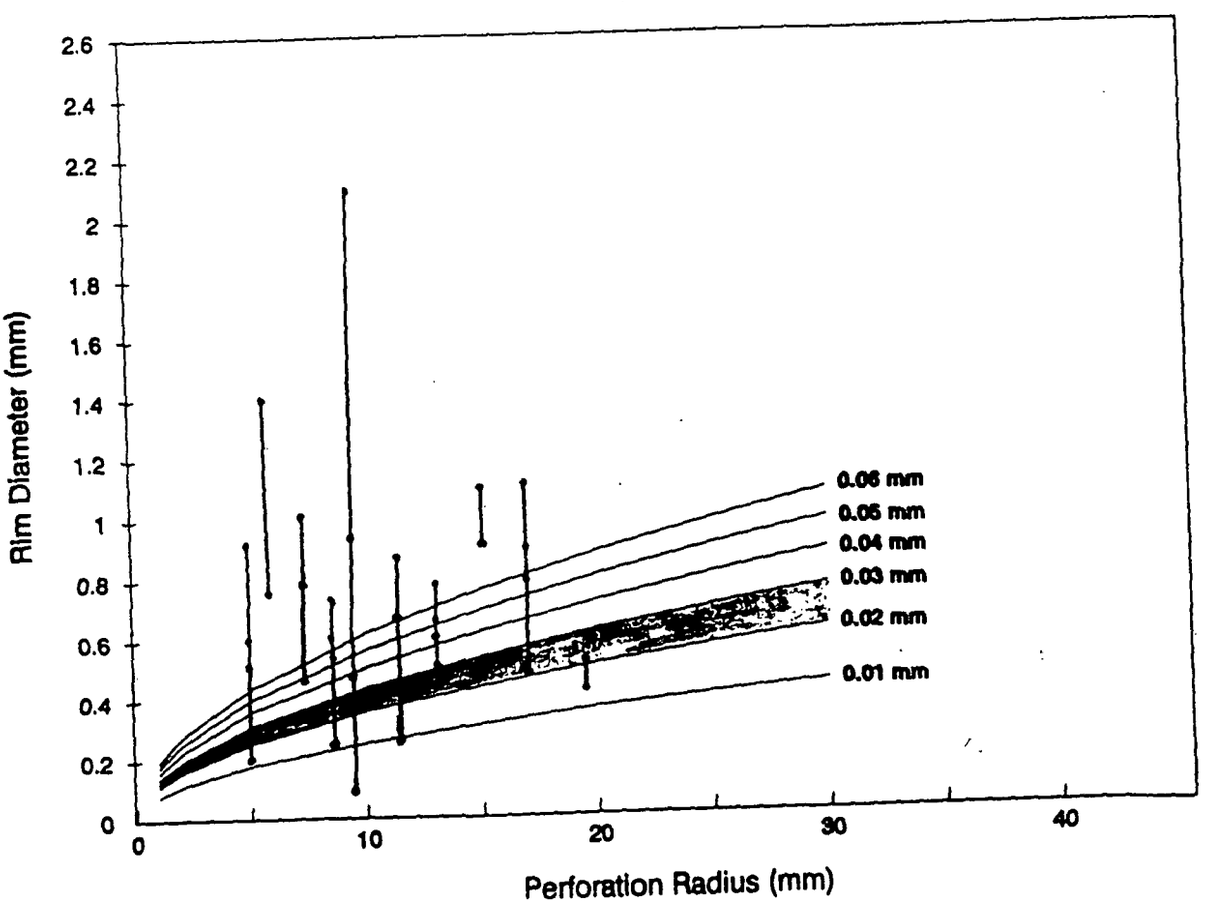
RIM THICKNESS

- mass balance for circular holes

$$d_L = \sqrt{(2R_p k_o / \pi R_d)}$$

d_L = diameter of the rim
R_p = perforation radius
R_d = distance from the origin
k_o = sheet attenuation constant

Rim Diameter versus Perforation Radius
for various sheet thicknesses



Strand break up:

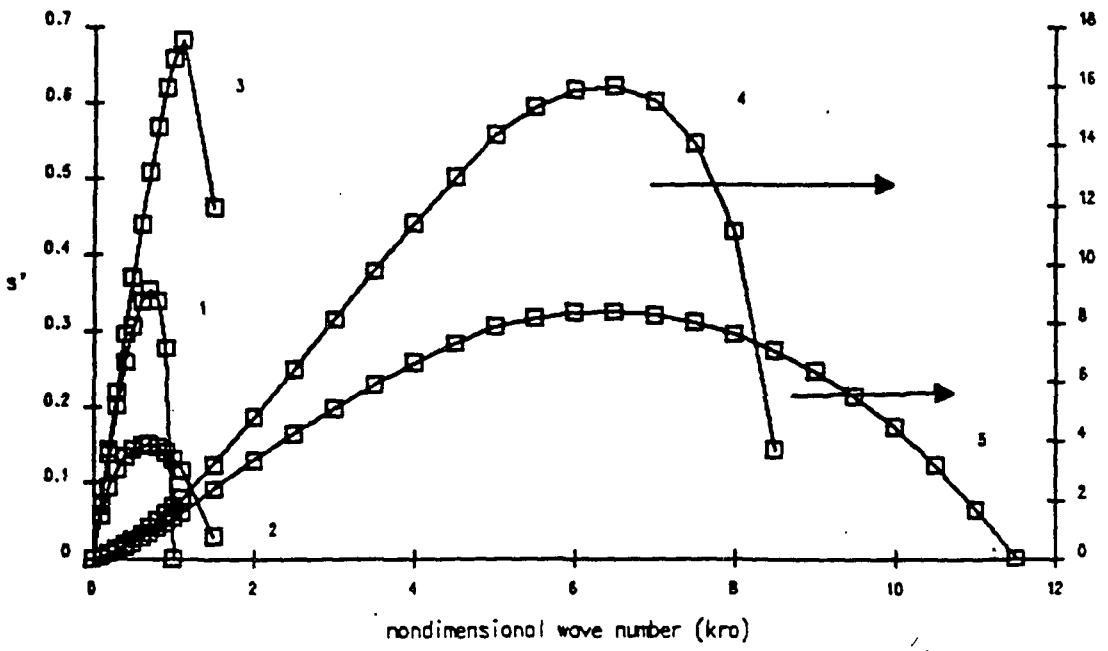
- wave growth
- inertial versus surface tension forces

Weber (1931)

- $\lambda_{max} = fn(We, Re, \rho_g/\rho_l)$
- $We = \rho_l V^2 Ro/\sigma$
- $Re = \rho_l V Ro/\mu$

variable	low	high	%Δ (Rd/Ro)
V (m/sec)	5.0	20	-53%
Ro (mm)	0.5	5.0	-52%
σ (dyne/cm)	24	72	+40%
ρ_g (kg/m3)	0.2	1.0	-39%
μ_l (cp)	20	400	+12%
ρ_l (kg/m3)	1000	1450	-1%

Dimensionless growth rate parameter as a function of dimensionless wave number, based on Weber's solution.



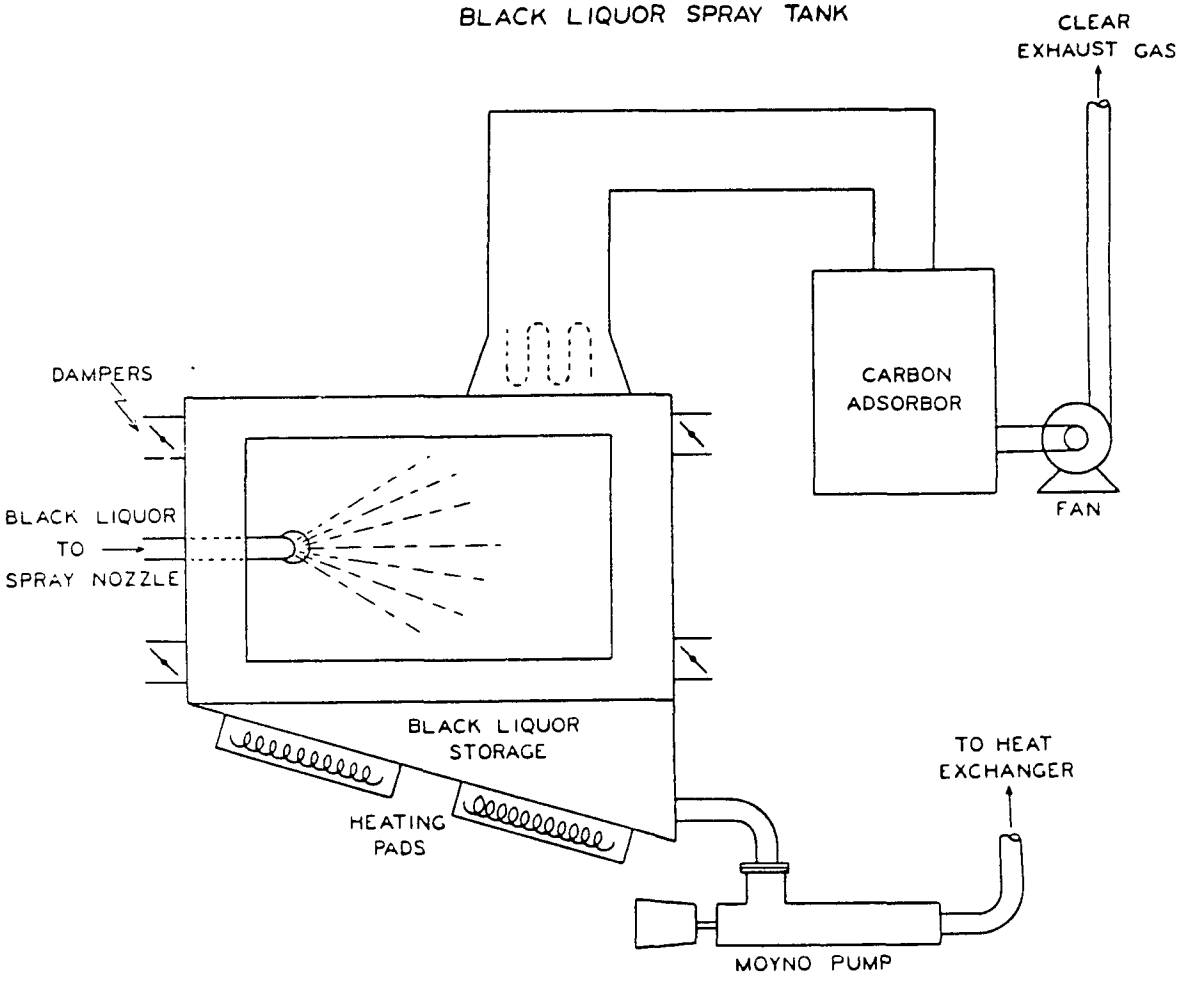
FUTURE WORK

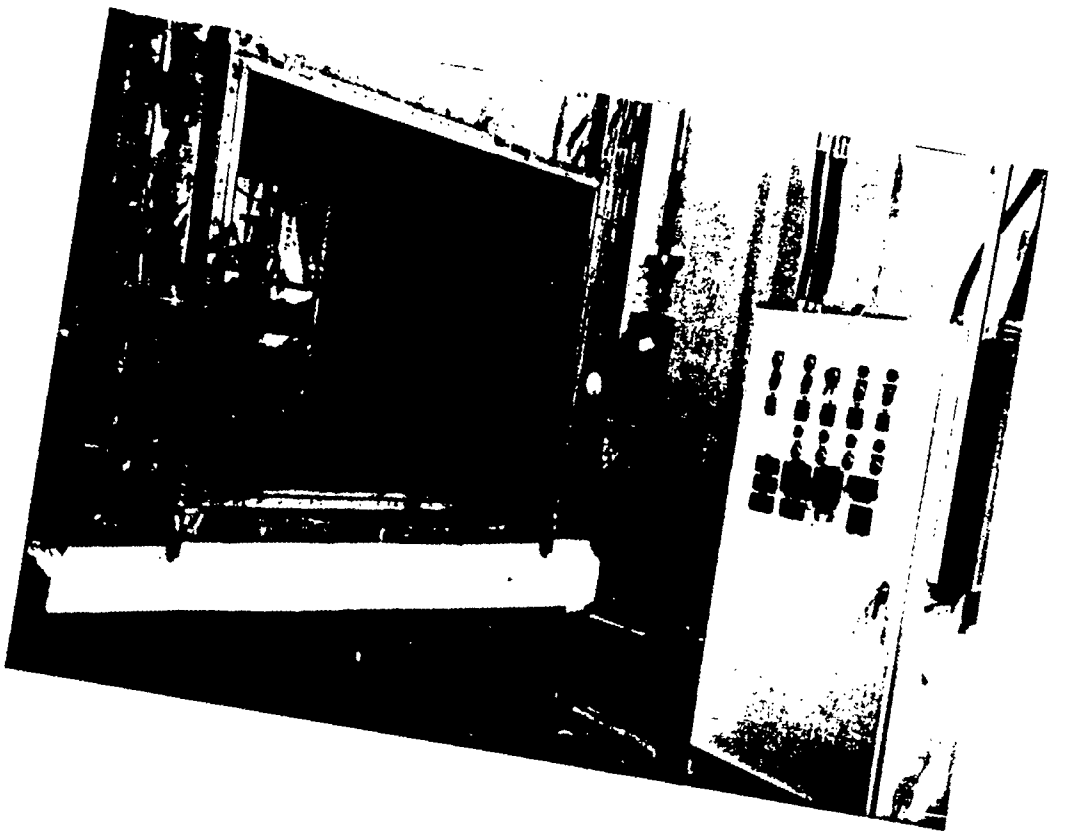
- Expand Perforation Number Density Data Base
- Correlate Number Density with Operating Conditions
- Determine Source of Perforations
- Develop Analytical Models

Black Liquor Delivery Systems
Project 3657-2
(DOE Funded)

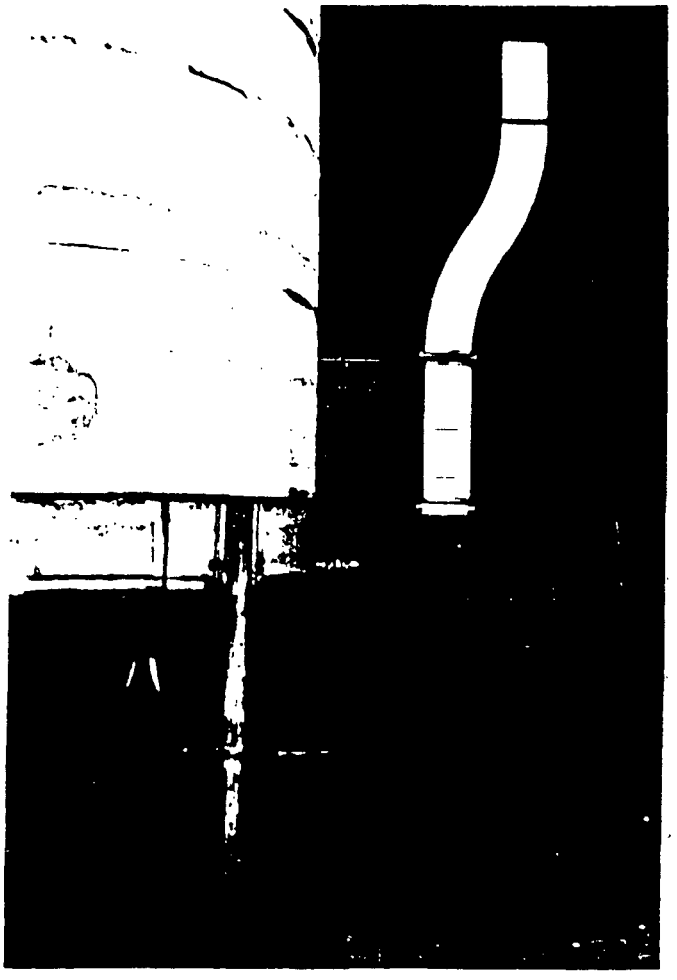
Steve Lien

PAC Meeting
December 14, 1990

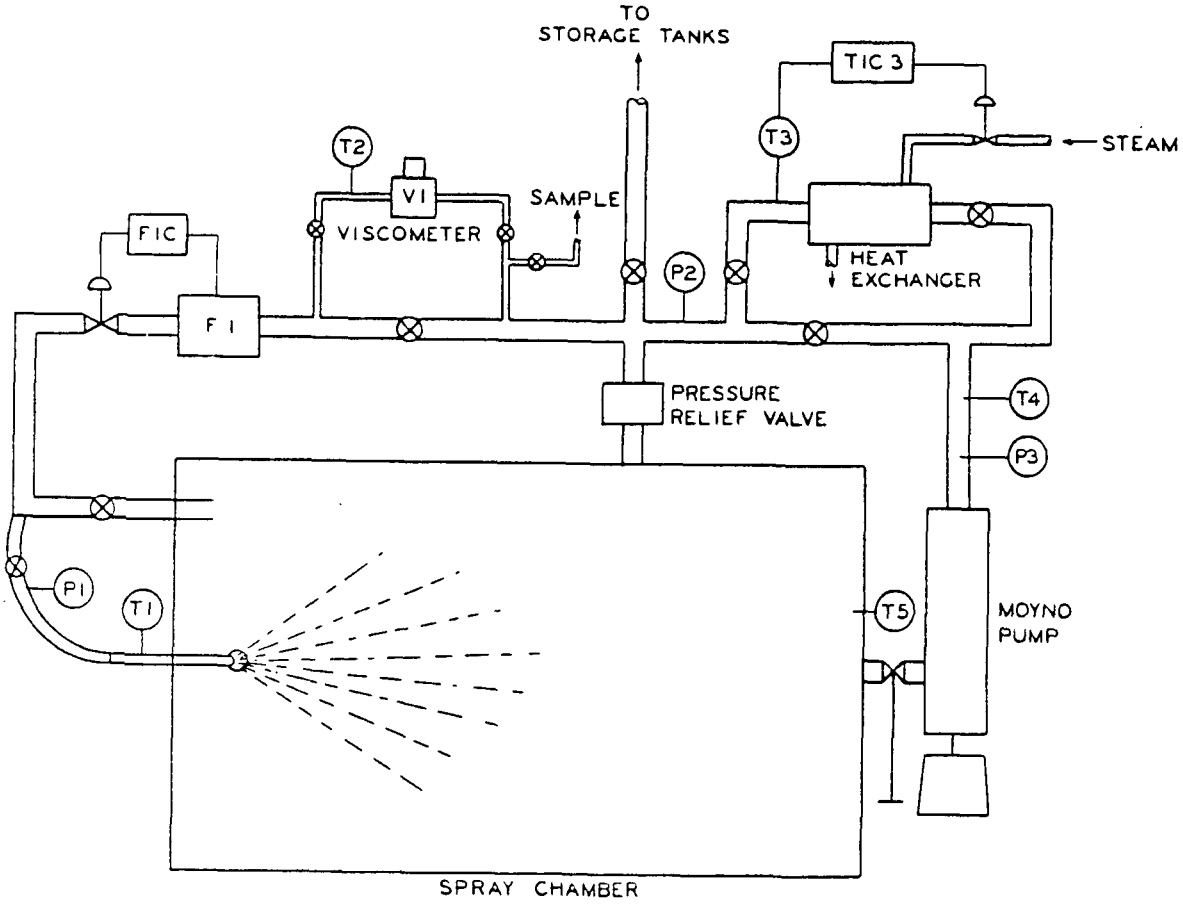

BLACK LIQUOR SPRAY TANK
CLEAR
EXHAUST GAS
CARBON
ADSORBOR
FAN
DAMPERS
BLACK LIQUOR
TO
SPRAY NOZZLE
BLACK LIQUOR
STORAGE
HEATING
PADS
TO HEAT
EXCHANGER
MOYNO PUMP



BLACK LIQUOR SPRAY TANK



CARBON ADSORBER



BLACK LIQUOR SPRAY TANK PIPING SCHEMATIC